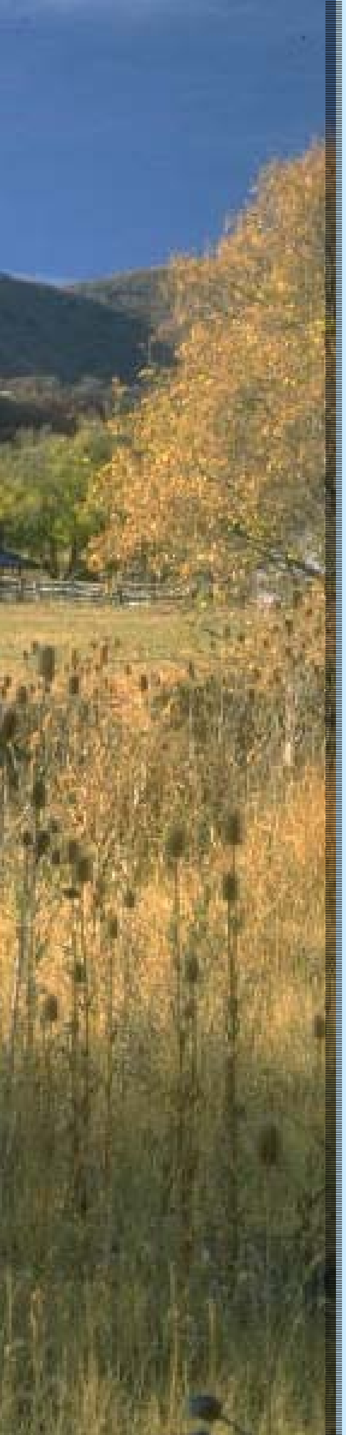


Estimating Times of Remediation Associated with Natural Attenuation

U.S. Geological Survey

Virginia Tech

Southern Division, NAVFACENGCOM

NAVFAC

Presentation Overview

- **Introduction**
- A Decision-Making Tool for Assessing MNA and Estimating Cleanup Times: Natural Attenuation Software (NAS)
- NAPL Dissolution Modeling with Sequential Electron Acceptor Model for 3D Transport (*SEAM3D*)
- Case Study
- Conclusions

Project Funding and Support

- YO817 project
- Initiated by **SOUTHDIV**
- Funded by **NAVFAC**
- Supported by **ARTT**

In the late 1980s, it was becoming clear that microbial biodegradation limited contaminant transport in groundwater systems

- Baedecker et al., 1988 (Bemidji, MN)
- Barker et al., 1987 (Borden field experiment). "Natural Attenuation of aromatic hydrocarbons in a shallow sand aquifer"
    - First use of term "natural attenuation"
    - Passive bioremediation, intrinsic bioremediation were other terms

By 1994, Natural Attenuation for petroleum contamination was getting regulatory acceptance

- U.S. EPA symposium on Intrinsic Bioremediation of Ground Water, 1994
- Wiedemeier et al., 1995, Air Force Fuels Protocol

After 1994, attention turned to chlorinated solvents

- U.S. EPA symposium on Natural Attenuation of chlorinated organics in groundwater, 1996.
- Wiedemeier/Air Force/EPA, 1998, "Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater"

EPA's Approach

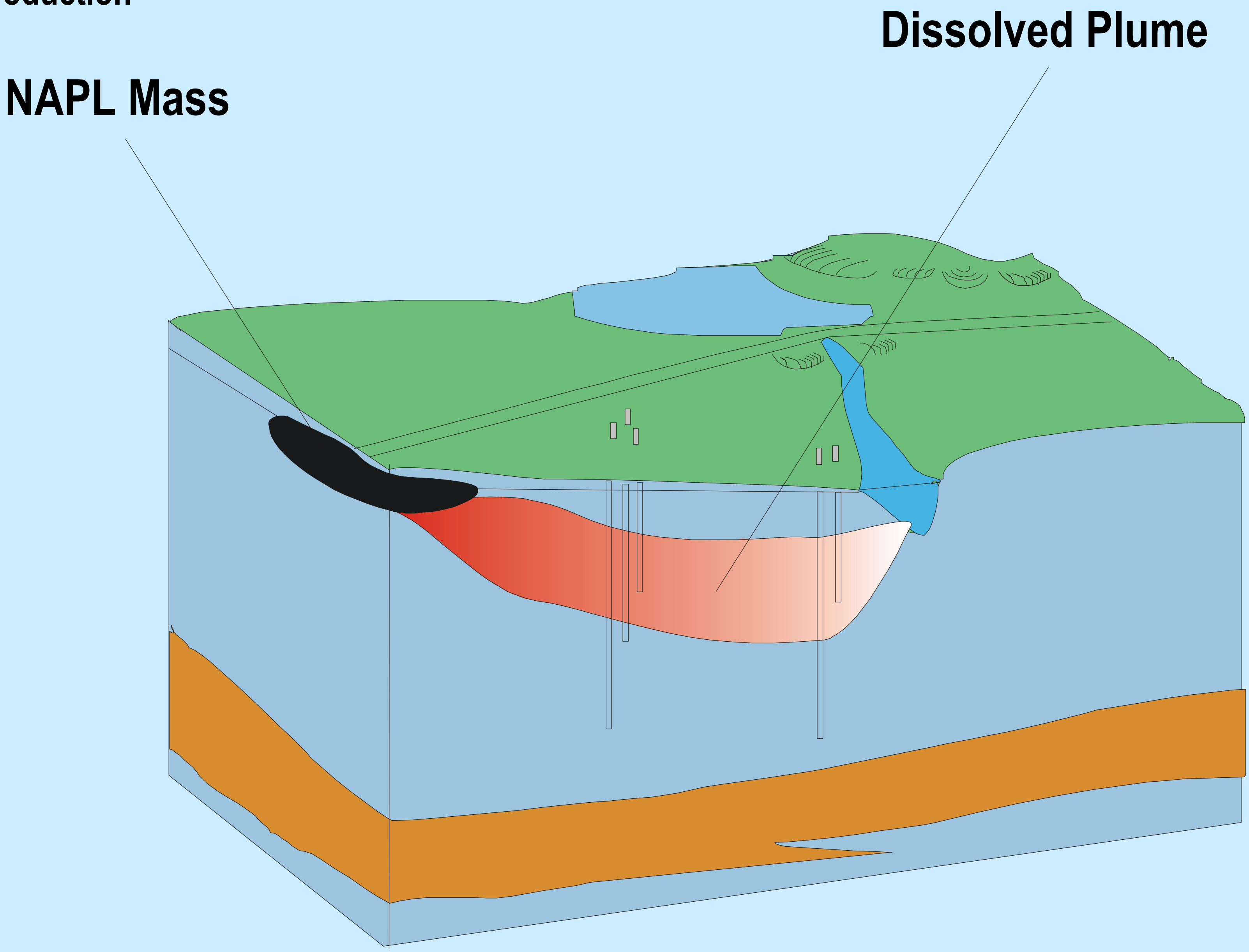
- According to the U.S. EPA, monitored natural attenuation can be selected as a remedial strategy **"only….where it will meet site remediation objectives within a timeframe that is reasonable compared to that offered by other methods."**

EPA OSWER Directive, 1999

This brought up the issue of Time of Remediation (TOR)

How do you estimate times of remediation?

- In 1999, there was no clear approach to this problem.


Dissolved Plume
NAPL Mass

TOR is a mass balance problem

$$M_o - (R_{MNA} * t)] = M_{remaining} \quad (1)$$

$$M_o - (R_{MNA} * t)] = M_{threshold} \quad (2)$$

$$t = [M_o - M_{threshold}]/R_{MNA} = TOR \quad (3)$$

M_0 = initial contaminant mass

$M_{remaining}$ = mass remaining after time t

R_{MNA} = mass removal due to MNA

There are many processes that contribute to contaminant removal (remediation by monitiored natural attenuation) [RMNA] in groundwater systems, including:

- Advection
- Dispersion
- Biodegradation
- Sorption
- NAPL Dissolution

Each of these components is summed up in the solute-transport equation

$$\frac{\partial C}{\partial t} = \underbrace{-v\frac{\partial C}{\partial x}}_{\text{Advection}} + \underbrace{D\frac{\partial^2 C}{\partial x^2}}_{\text{Dispersion}} - \underbrace{\frac{K_d \rho_b}{n}\frac{\partial C}{\partial t}}_{\text{Sorption}} - \underbrace{R_{bio}}_{\text{Biodegradation}} + \underbrace{R_{NAPL}}_{\text{NAPL Dissolution}}$$

Solving this equation to obtain meaningful TOR estimates, however, is not an easy problem

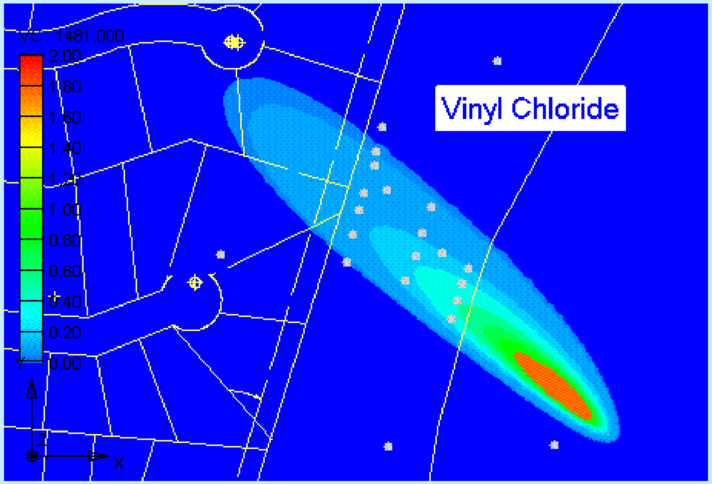
$$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - \frac{K_d \rho_b}{n}\frac{\partial C}{\partial t} - R_{bio} + R_{NAPL}$$

To facilitate finding useful solutions, the TOR problem can be divided into three interactive components:

- Distance of Plume Stabilization
- Time of Plume Stabilization
- Time of NAPL Dissolution

Distance of Stabilization (DOS)

How far will it go?

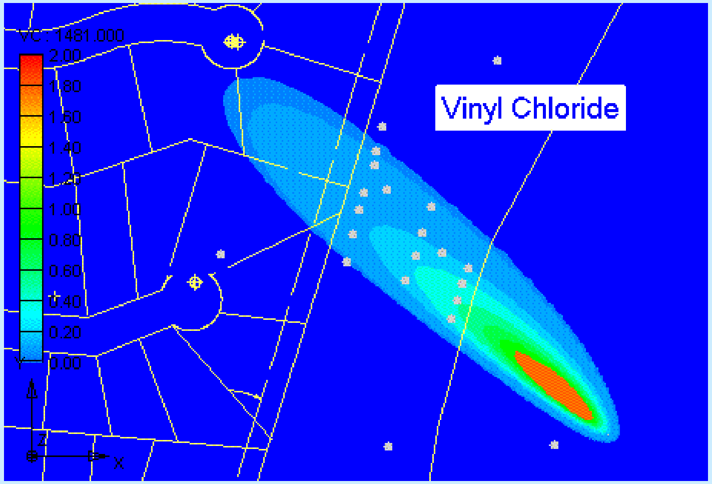


High-concentration Source, Impacting Sensitive Receptors

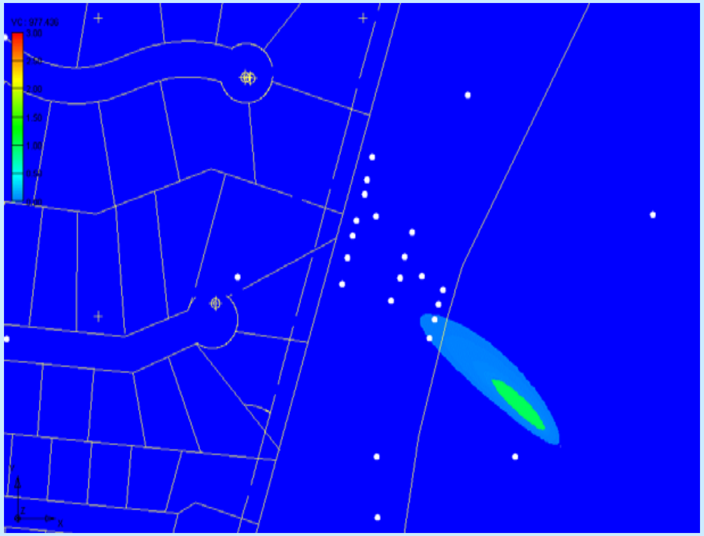
Lower Concentration Source, Not Impacting Sensitive Receptors

Time of Stabilization (TOS)

How long will it take?



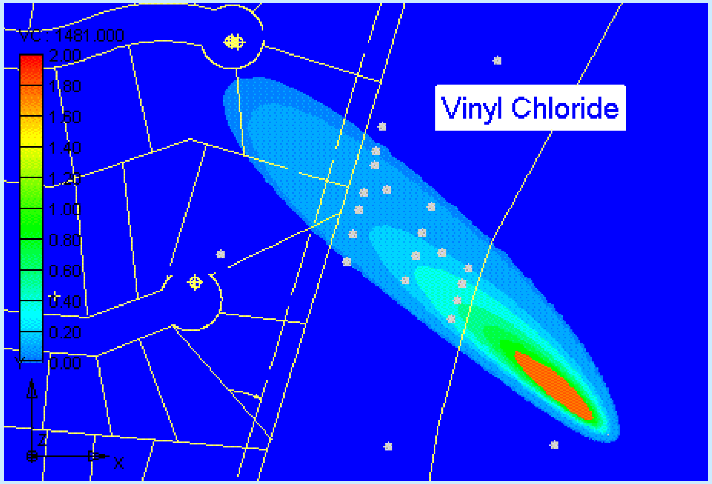
Source Area Removal, 1998



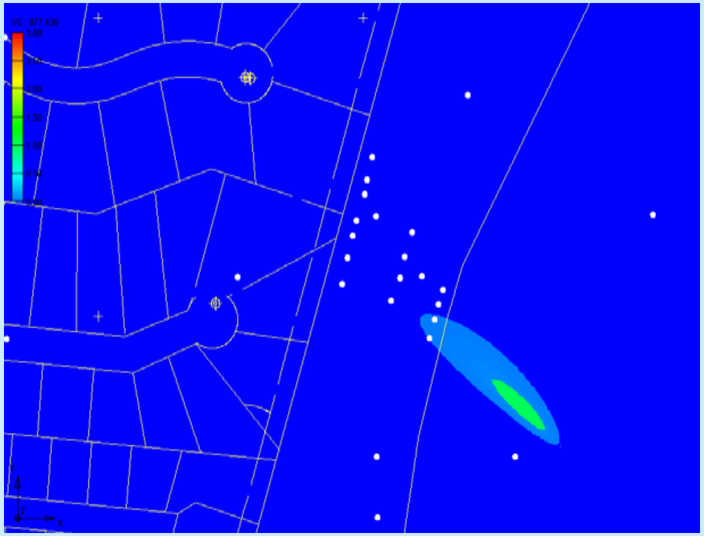
Collapsed Contaminant Plume, 2005? 2050?

Time of NAPL Dissolution (TNAD)

How long will it take?



PCE Source Area
Emplaced 1960



Source PCE
Fully Dissolved
2005?
2050?

Analytical and Numerical Solutions for Solving the Mass-Balance TOR Problem

- Distance and Time of Plume Stabilization
  - Analytical; Domenico, 1987
- Time of NAPL Dissolution
  - Numerical – *SEAM3D*; Waddill and Widdowson, 2000

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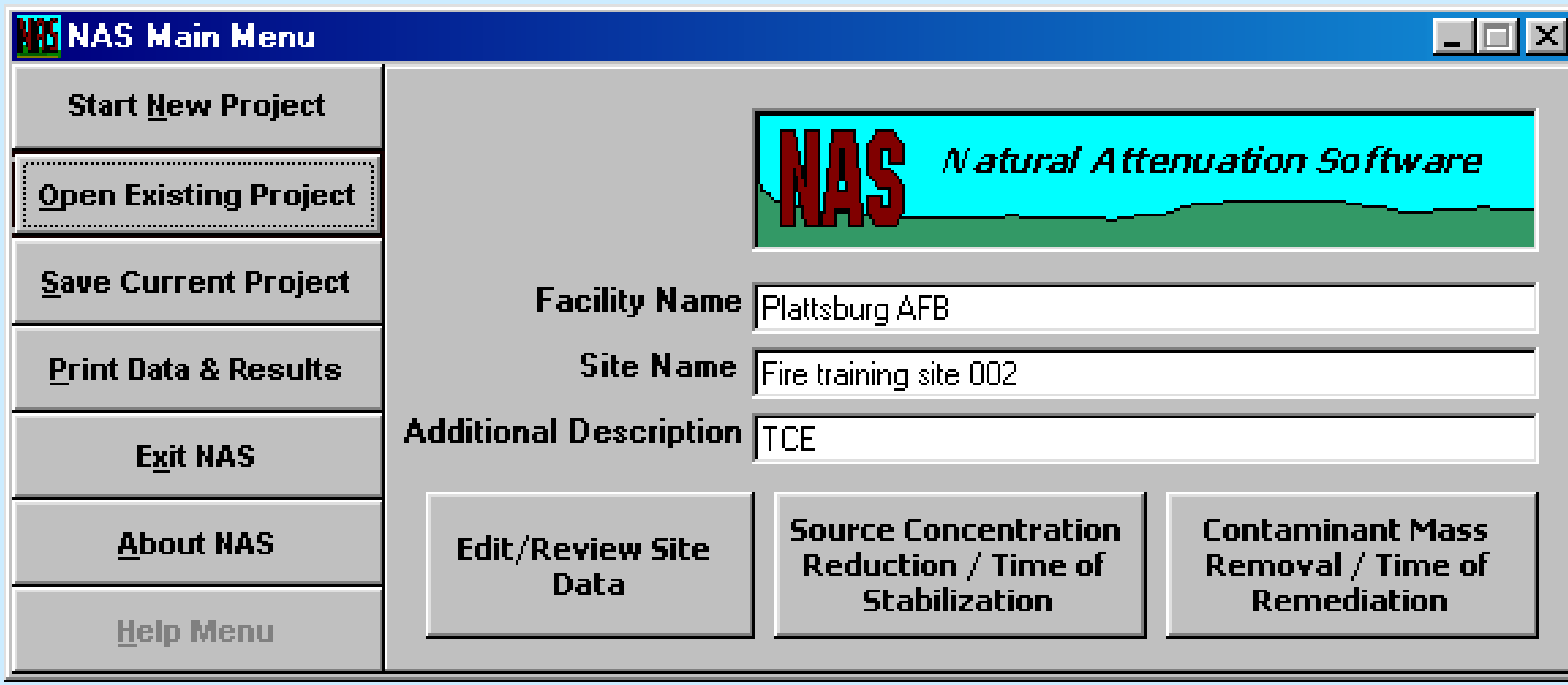
Introduction to NAS



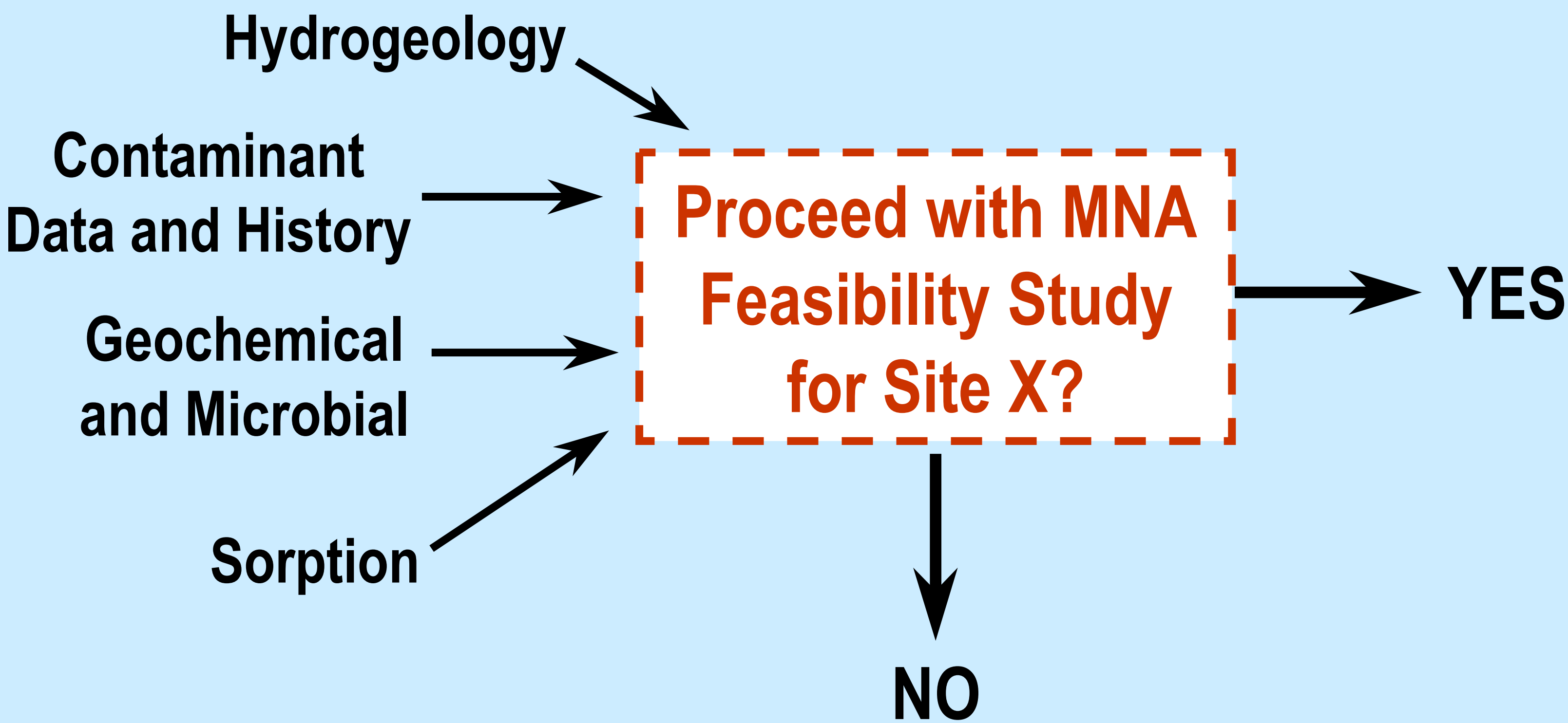
A Decision-Making Tool for Assessing Monitored Natural Attenuation and Estimating Cleanup Times

Department of Civil and Environmental Engineering

U.S. Geological Survey
WRD Columbia, SC

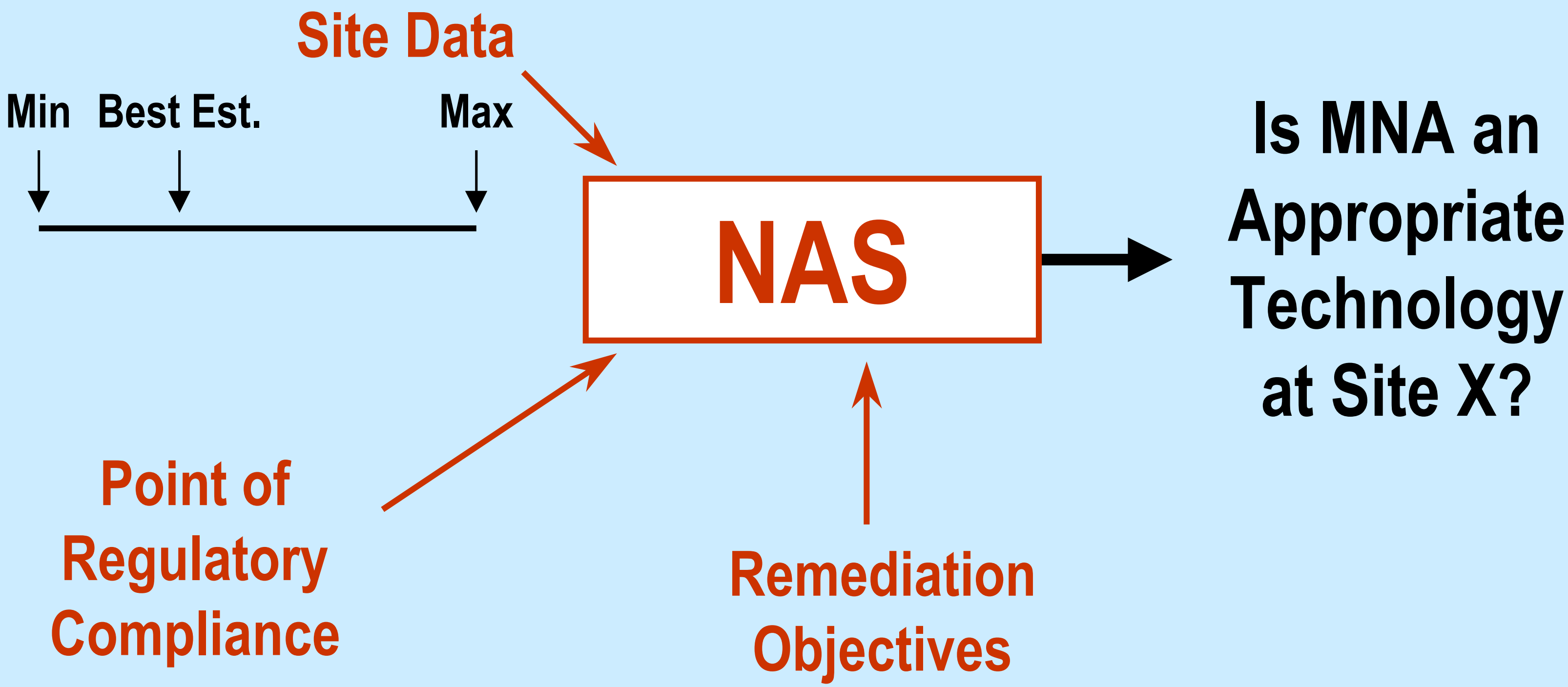
NA Screening Tools

Monitored Natural Attenuation (MNA)



NAS – A Tool for Decision-Making

Monitored Natural Attenuation (MNA)



NAS – Questions Addressed

- **Is MNA an appropriate technology at Site X?**

  <u>and</u>

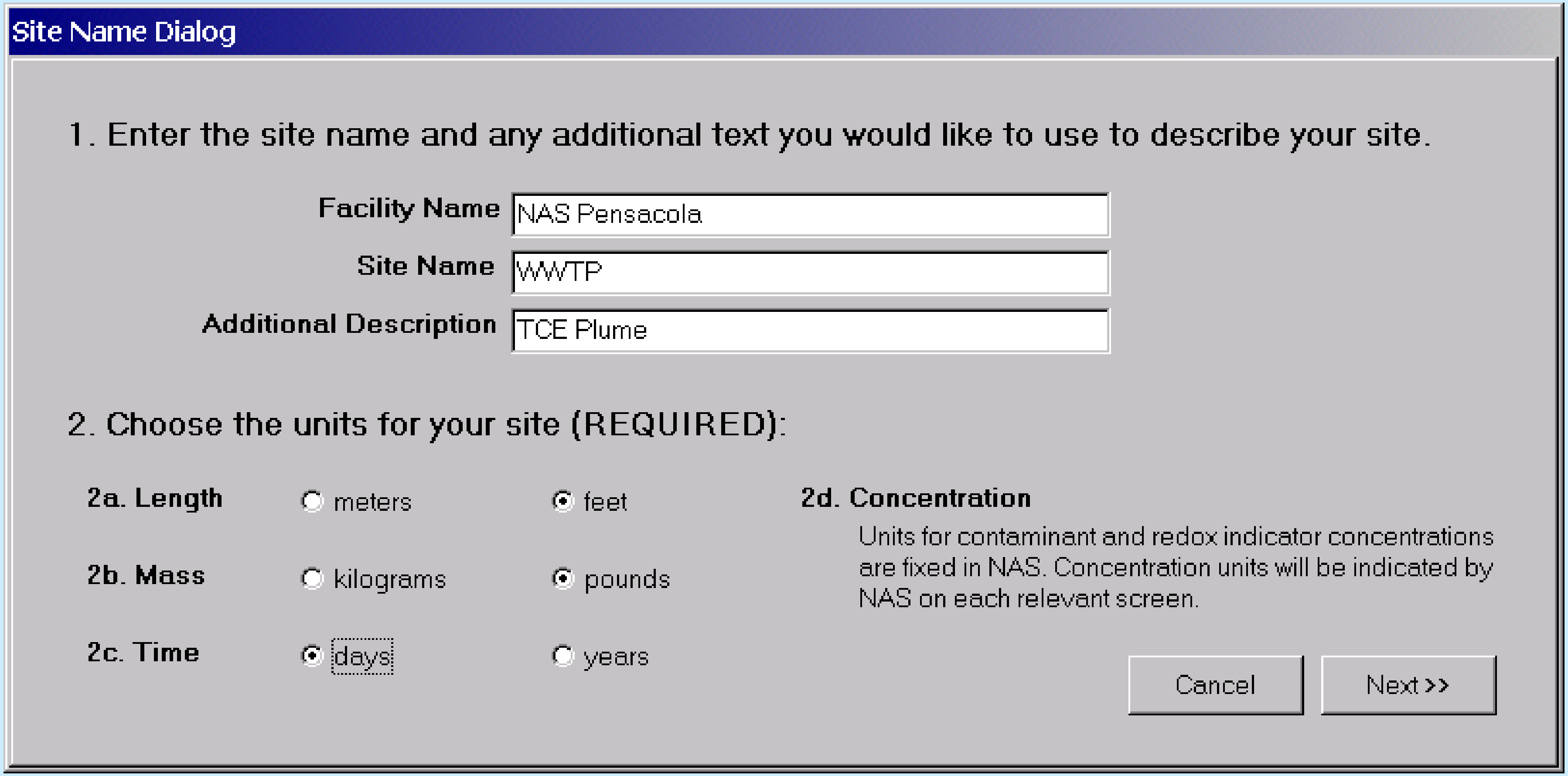
  What degree of source remediation is required at Site X?

  - Distance of Plume Stabilization
  - Time of Plume Stabilization
  - Time of NAPL Dissolution

NAS – Types of Problems and Source Contaminants

- **Chlorinated Ethenes**
  - PCE or
  - TCE
- **Petroleum Hydrocarbons**
  - BTEX
  - MTBE (optional)
  - Naphthalene (optional)

NAS – Site Name Dialog



Chlorinated Ethene Sites

Contaminant Source

Choose the type of contaminants found at your site

- ○ Petroleum Hydrocarbon (e.g. Gasoline, Jet Fuel, Fuel Oil)
- ◉ Chlorinated Ethenes (PCE or TCE)

Choose Source Parent Compound

- ○ PCE Source
- ◉ TCE Source

Simulated Contaminants	Solubility (mg/L)	Molecular Weight (g/mol)
TCE	1100	131.5
cis-DCE	800	97
Vinyl Chl.	2670	62.5

Next >>

Cancel

Petroleum Hydrocarbon Sites

Contaminant Source

Choose the type of contaminants found at your site

- (•) Petroleum Hydrocarbon (e.g. Gasoline, Jet Fuel, Fuel Oil)
- ( ) Chlorinated Ethenes (PCE or TCE)

Choose to include MTBE and Naphthalene

Include MTBE? (•) Yes ( ) No

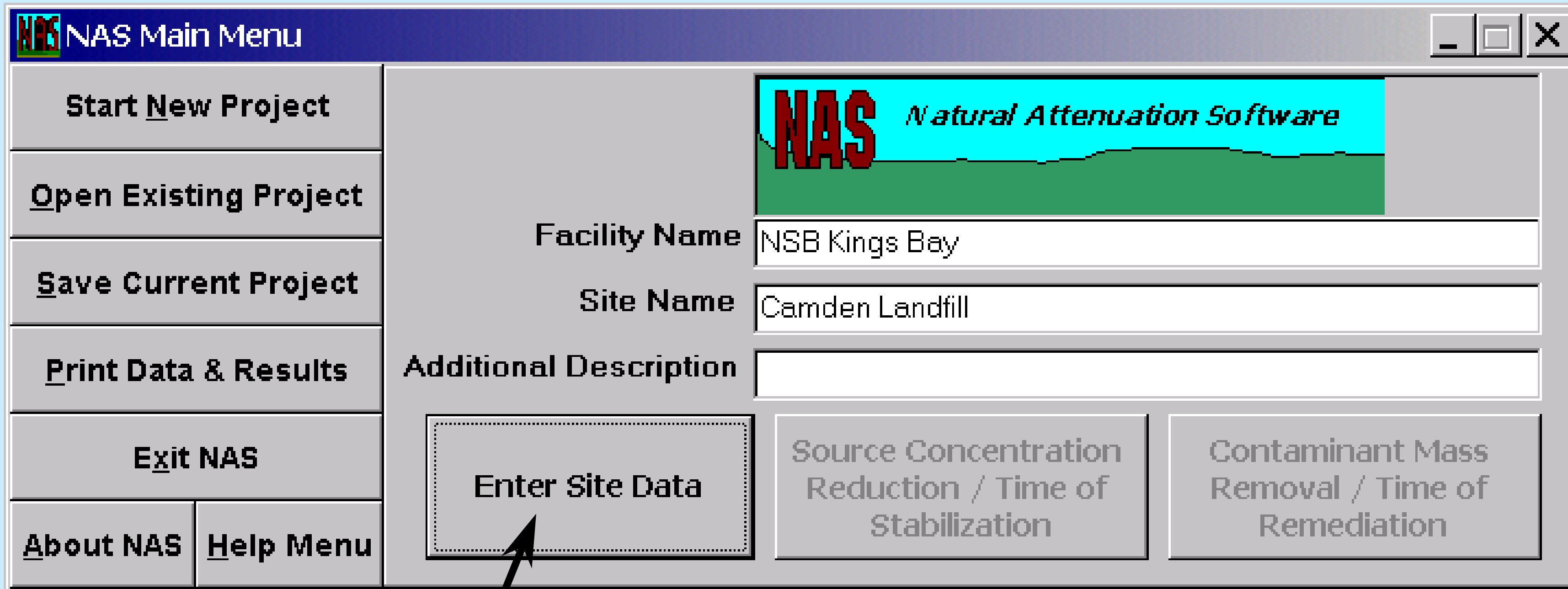
Include Naphthalene? ( ) Yes (•) No

Simulated Contaminants	Solubility (mg/L)	Molecular Weight (g/mol)
Benzene	1750	78.1
Toluene	535	92.1
Ethylbenzene	152	106.2
Xylene	175	106.2
MTBE	48000	88.2

Next >>

Cancel

NAS – Site Data Assessment



Site Data Assessment
(Identification of Terminal Electron-Accepting Process [TEAP] Zones and Natural Attenuation Capacity [NAC] Calculation)

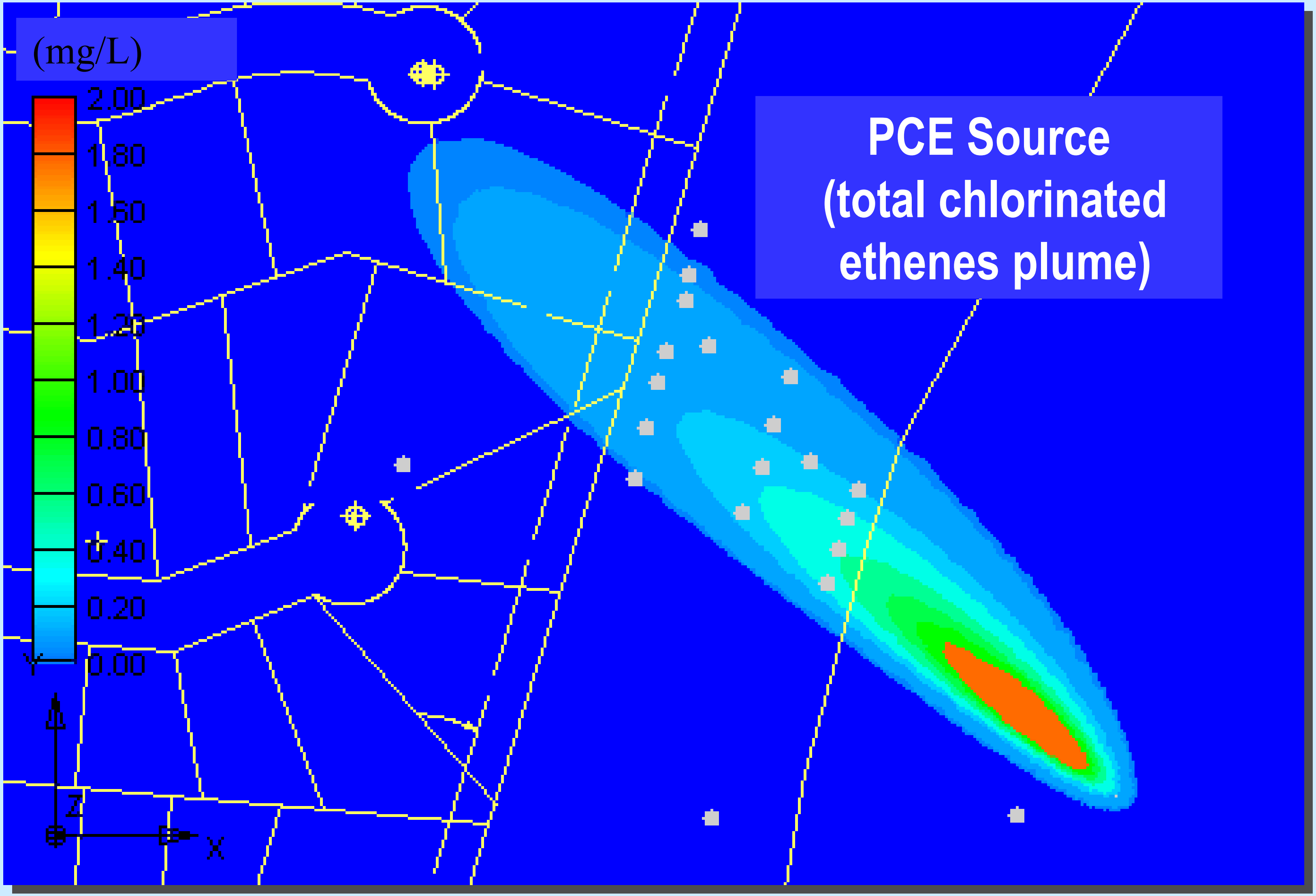
NAS – Site Data Assessment

Goal:
Determine contaminant degradation rates and redox zonation

Data Requirements

- Hydrogeologic data
- Contaminant concentrations
- Redox indicator concentrations
- Sorption characteristics

NAS Example –
Naval Submarine Base Kings Bay, GA



NAS Example – NSB Kings Bay, GA

Site Information

Site Information

Hydrogeology Data | Contaminant Data | Redox Indicator Data | Site Data Summary | Graphical Summary

1. Enter the following hydrogeologic and aquifer properties.

	Maximum	Average	Minimum
Hydraulic Conductivity [ft/yr]	3600.0	1440.0	720.0
Hydraulic Gradient [ft/ft]	0.048	0.048	0.048
Weight Percent Organic Matter (loss on ignition) [%]	0.19	0.19	0.19

	Average
Total Porosity [ft³/ft³]	0.25
Effective Porosity [ft³/ft³]	0.25
Contaminated Aquifer Thickness [ft]	20.0

Return To Main Menu

$$v = \frac{K}{Rn_e} i$$

NAS

Site Information

Hydrogeology Data | **Contaminant Data** | Redox Indicator Data | Site Data Summary | Graphical Summary

1. Enter the date when field measurements for contaminant concentration were collected:

Month November **Year** 1999

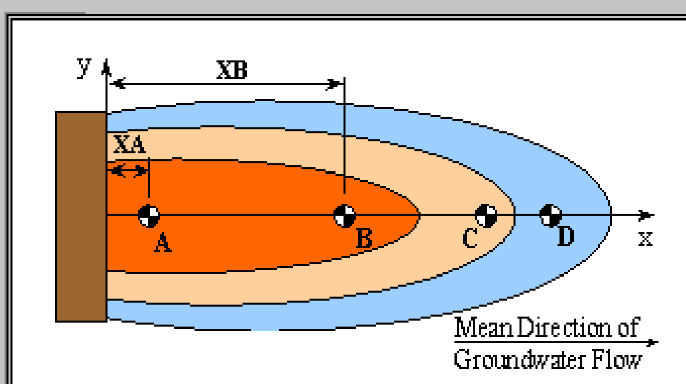
2. Enter the number of monitoring wells sampled for contaminant concentration along the centerline of the plume:

Currently, contaminant concentation data is reported for 6 wells.

Add/Delete Wells

3. Enter the well name (optional), distance downgradient of the source (required), and contaminant concentrations measured at each monitoring point.

Well Name	Distance from Source [ft]	PCE [µg/L]	TCE [µg/L]	cis-DCE [µg/L]	VC [µg/L]
KBA-34	1.	3500.	1000.	BD	BD
usgs-3	110.	2.	511.	1270	112
KBA-13	160.	0.5	32.5	158	76
usgs-5	220.	BD	BD	54	166
usgs-10	380.	BD	BD	24	31
KBA-37	630.	BD	BD	10	2



NOTE: The origin of the NAS coordinate system (0,0) is located immediately downgradient of the area and along the centerline of the plume.

Return To Main Menu

NAS

Site Information

Hydrogeology Data | Contaminant Data | **Redox Indicator Data** | Site Data Summary | Graphical Summary

1. Enter the time when the redox indicator field measurements were collected:

- (•) **November 1999 (Collected at the same time as contaminant data.)**
- ( ) **Collected at a different time than contaminant data**

Month November **Year** 1999

2. NAS requires specification of dissolved oxygen (O2), ferrous iron (Fe2) and sulfate (SO4) at all redox well locations. Indicate which additional redox indicators were measured at your site:

Nitrate (NO3):	☑ **Yes**	☐ **No**
Manganese(II) (MN2):	☐ **Yes**	☑ **No**
Hydrogen Sulfide (H2S):	☑ **Yes**	☐ **No**
Methane(CH4):	☑ **Yes**	☐ **No**
Hydrogen (H2):	☑ **Yes**	☐ **No**

3. Number of redox indicators along the centerline of the plume.

Currently, redox indicator concentration data is reported for 6 wells. **Add/Delete Wells**

4. Enter the well name (optional), distance downgradient of the source (required), and concentrations for indicators of redox potential measured at each monitoring point.

Well Name	Distance from Source [ft]	O2 (mg/L)	NO3 (mg/L)	Fe2 (mg/L)	S04 (mg/L)	H2S (mg/L)	CH4 (mg/L)	H2 (nM)	Redox Condition
KBA-34	1.	0	0	1	10	0	5	2	SO4/CO2-reducing
usgs-3	110.	0	0	0.39	6.48	0	3.8	1.66	SO4/CO2-reducing
KBA-13	160.	0	0	0.24	3.27	0.577	5.1	1.55	SO4/CO2-reducing
usgs-5	220.	0	0	0.26	0	0.385	5.6	0.5	Ferrogenic
usgs-10	380.	0	0	0.41	10	1.5	6	0.81	Ferrogenic
KBA-37	630.	0	0	0.3	10.2	0.1	0.3	0.3	Ferrogenic

Update Redox Condition | Return To Main Menu

NAS

Site Information

Hydrogeology Data | Contaminant Data | Redox Indicator Data | **Site Data Summary** | Graphical Summary

Facility Name NSB Kings Bay

Site Name Old Camden Landfill

Additional Description PCE Site

Unit Specification

Length = feet

Time = years

Mass = pounds

Solute Transport Parameters

ADVECTION

	High	*Best Est.*	*Low*	*Units*
1. Hydraulic Conductivity:	3000.	2500.	2000.	[ft/yr]
2. Hydraulic Gradient:	0.006	0.005	0.004	[ft/ft]
3. Porosity (Best Estimate):		0.25		[ft^3/ft^3]
4. Groundwater Velocity:	72.	50.	32.	[ft/yr]

DISPERSION

	Units
1. Estimated Plume Length:	845.9 [ft]
2. Longitudinal Dispersivity:	22.79 [ft]
3. Dispersivity Ratio:	20.0 [-]

SORPTION

View Retardation Factors

BIODEGRADATION

View NAC & Decay Rates

Geochemical Concentration Data

Contaminant Concentrations (November 1999)

Well Name	Distance from Source [ft]	PCE [µg/L]	TCE [µg/L]	cis-DCE [µg/L]	VC [µg/L]
KBA-34	1.	3500.	1000.	BD	BD
usgs-3	110.	2.	511.	1270	112
KBA-13	160.	0.5	32.5	158	76
usgs-5	220.	BD	BD	54	166
usgs-10	380.	BD	BD	24	31
KBA-37	630.	BD	BD	10	2

Return To Main Menu

Distance and Time of Stabilization Demonstration

Open NAS and give demonstration of DOS and TOS calculations for Cecil Field

Presentation Overview

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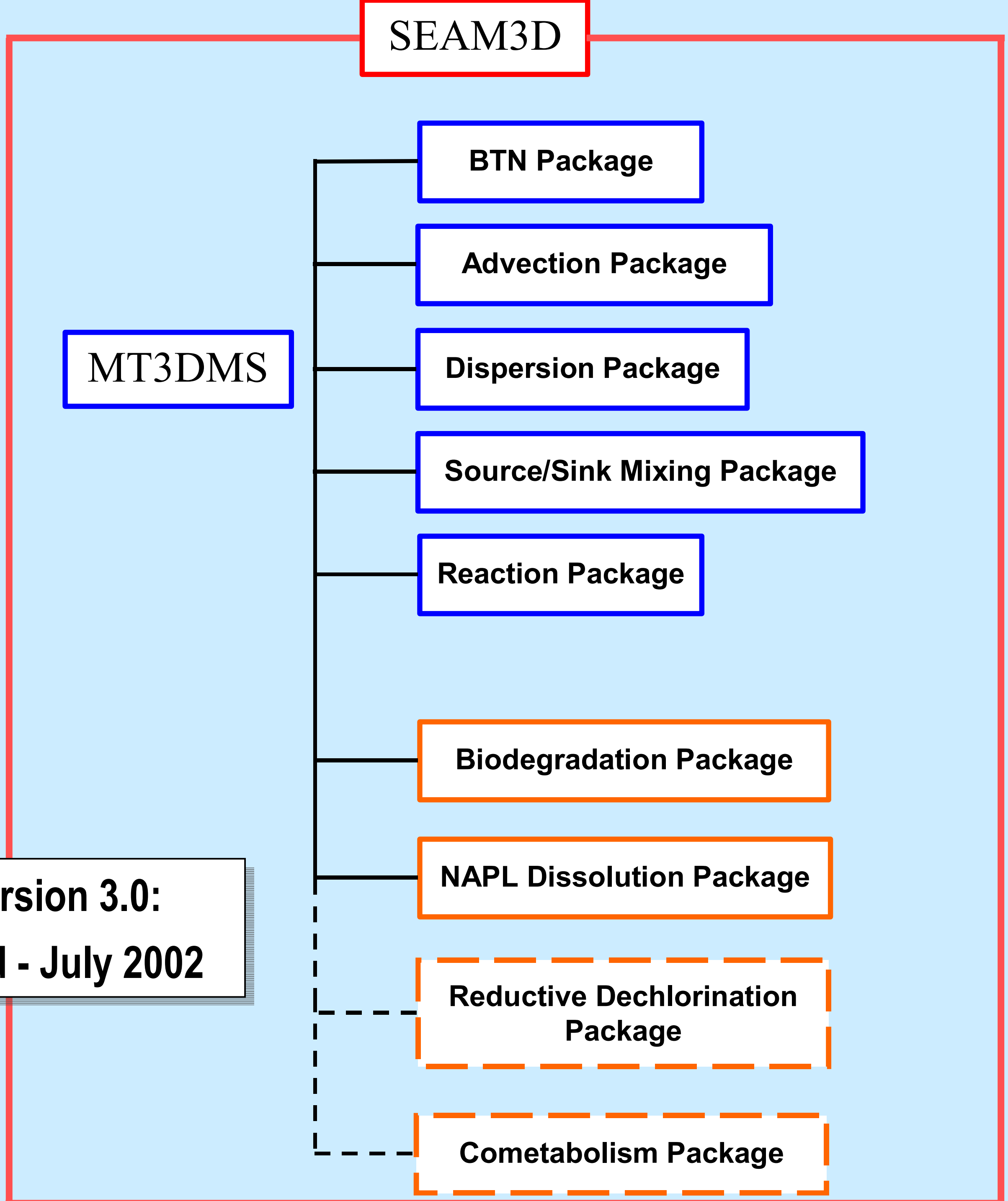
NAPL Dissolution Modeling with Sequential Electron Acceptor Model for 3D Transport (*SEAM3D*)

Department of Civil and
Environmental Engineering

U.S. Geological Survey
WRD Columbia, SC

SEAM3D

- Sequential Electron Acceptor Model for 3D Transport
- Simulates both aerobic and anaerobic biodegradation of contaminants in groundwater
- Designed for application to:
  - Engineered bioremediation systems
  - Intrinsic bioremediation (natural attenuation)



SEAM3D version 3.0:

- Released - July 2002

SEAM3D
Governing Equations

- Hydrocarbon Compounds: S_{ls} *(ls=1, 2, …, NH)*

NH = number of hydrocarbon compounds specified by model users

$$-\frac{\partial}{\partial x_i}\left(\bar{v}_i S_{ls}\right)+\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial S_{ls}}{\partial x_j}\right)+\frac{q_s}{\theta}S_{ls}^{*}-R_{\sin k,ls}^{bio}+R_{source,ls}^{NAPL}=R_{ls}\frac{\partial S_{ls}}{\partial t}$$

Advection

Dispersion

Fluid Source/Sink

Biodegradation Reaction Term

NAPL Dissolution Source Term

Retardation Factor

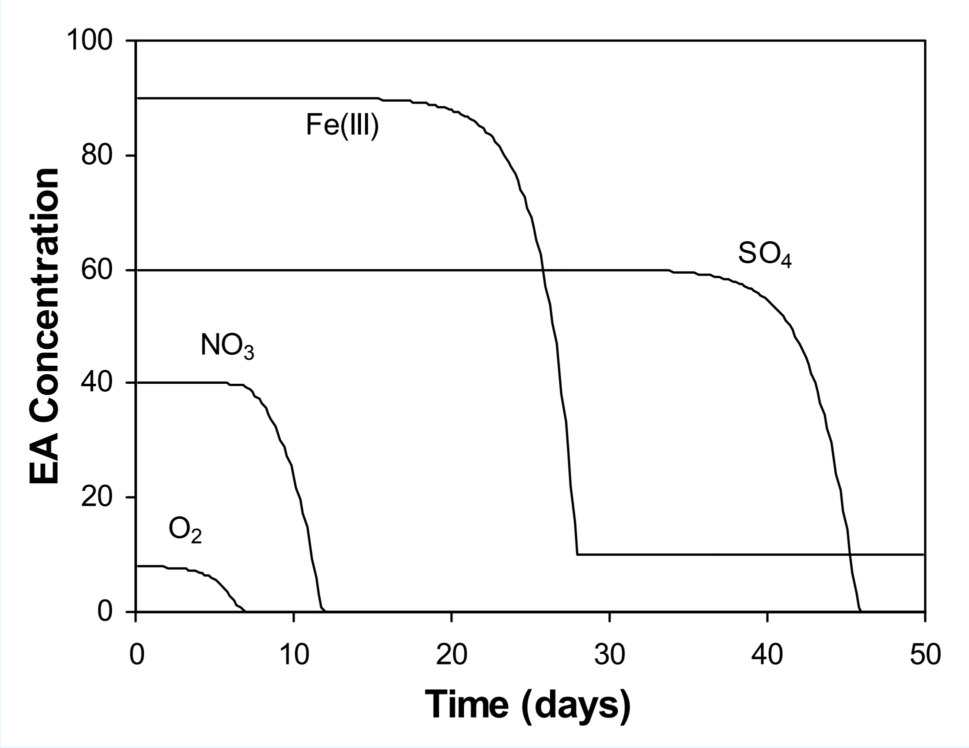
SEAM3D

Sequential TEAPs

- EA Inhibition Function - prevents anaerobic TEAPs from operating in the presence of higher-energy electron acceptors:

$$I_{le,li} = \prod_{li=1}^{le-1} \left[\frac{\kappa_{le,li}}{\kappa_{le,li} + \overline{E}_{li}} \right]$$

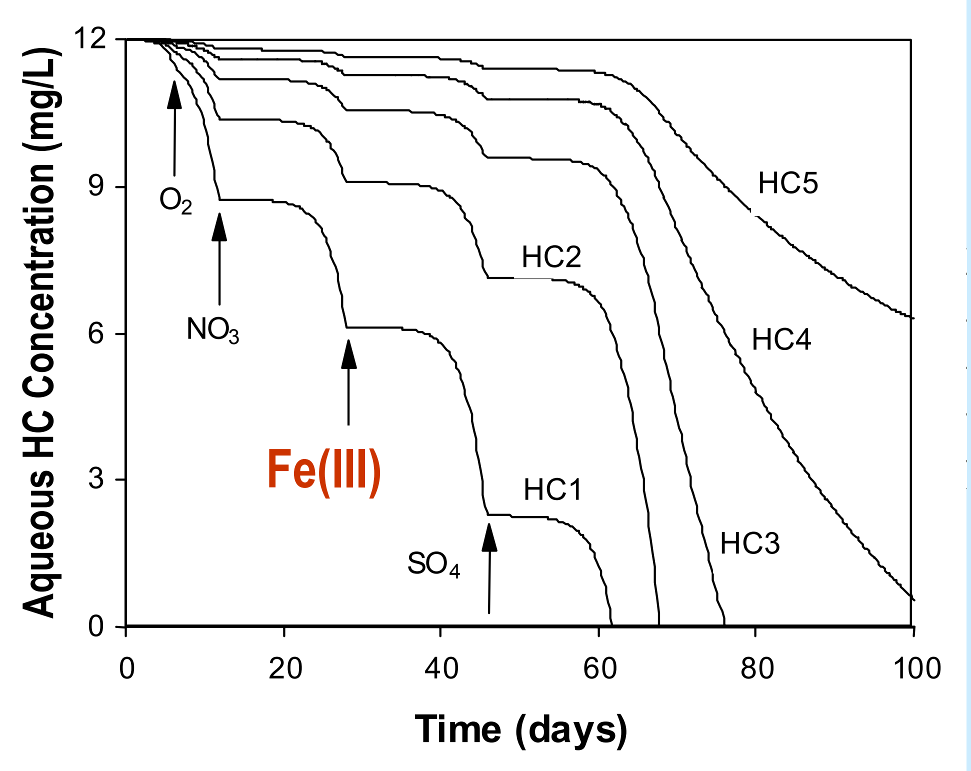
for *le* = 2, 3, 4, 5, 6



***SEAM3D* prediction of electron acceptor (EA) concentrations, showing that utilization of each EA is inhibited until the preceding EA has been depleted.**

SEAM3D
Hydrocarbon Biodegradation

- Hydrocarbon Biodegradation – BTEX loss may be simulated using utilization rates varying by compound and TEAP



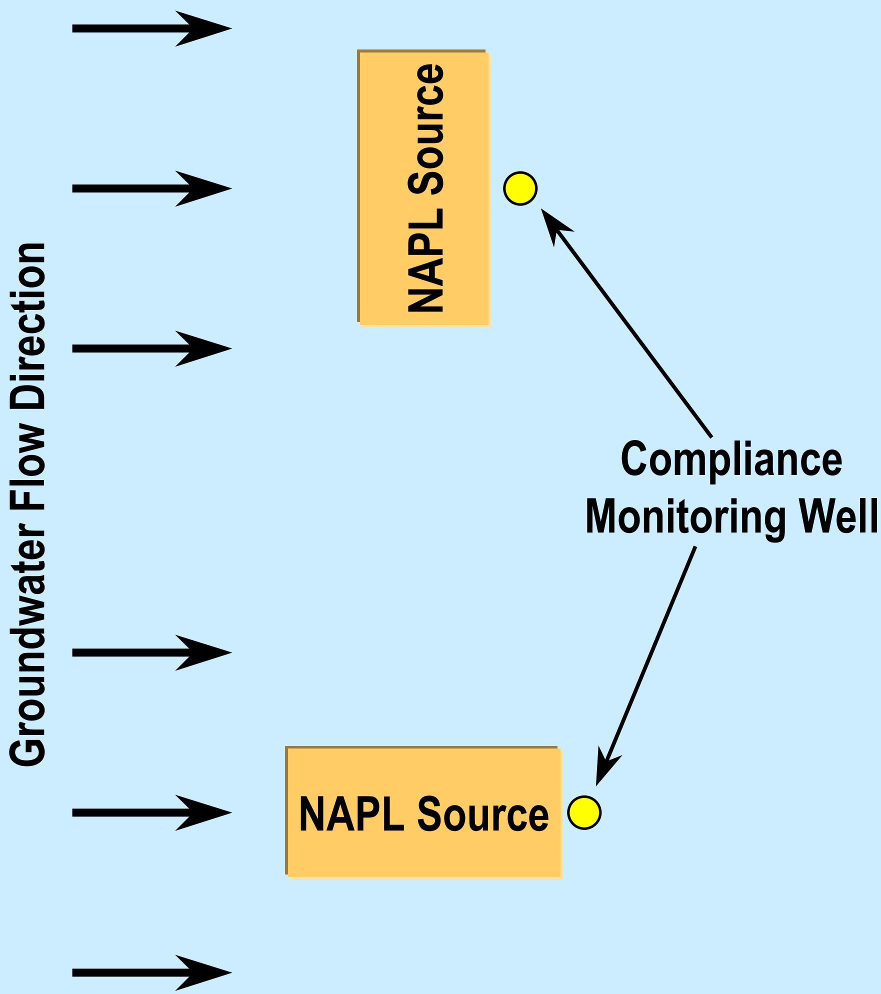
SEAM3D **prediction of five hydrocarbon (HC) substrate concentrations, showing the effect of varying the maximum specific rate of substrate utilization. Arrows indicate the termination of each electron acceptor process.**

Factors Affecting NAPL Dissolution

<u>NAPL Properties</u>

- NAPL mass
- Residual saturation
- Contaminant mass fraction
- Physical properties of NAPL components
- NAPL dissolution coefficient (k^{NAPL})
- Source geometry

Source Geometry



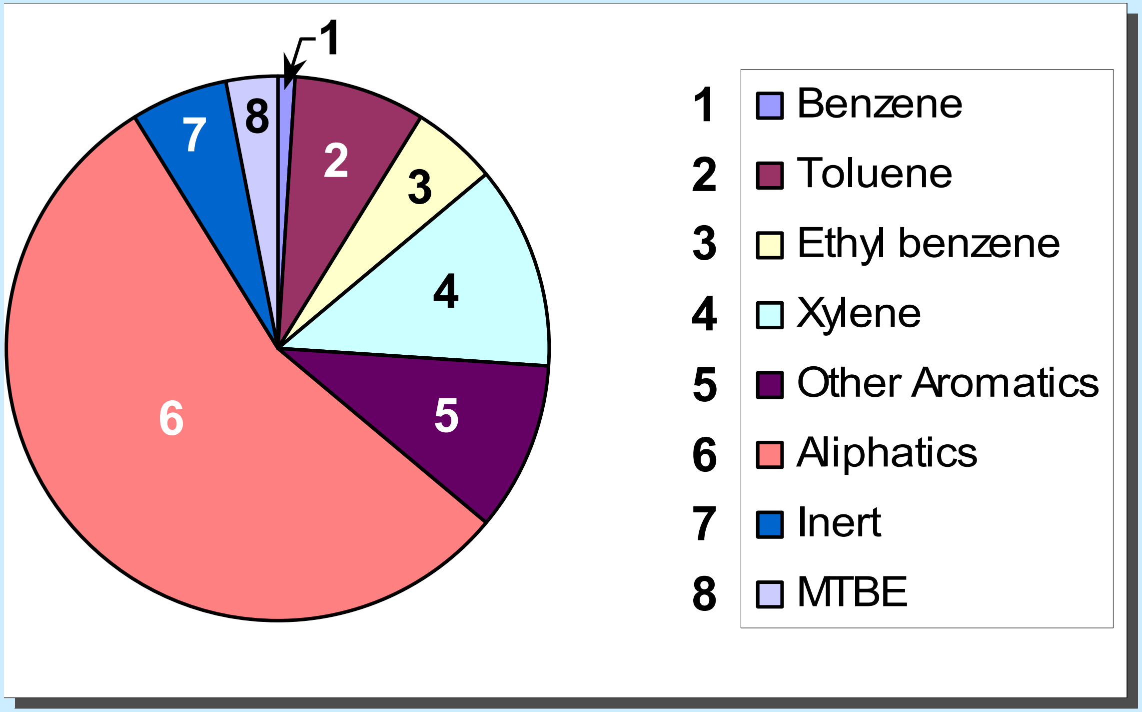
- For these two cases and with all things being equal, except the orientation of the source relative to the groundwater flow direction, would source geometry influence TOR?

- If the answer is yes, which case would result in the greater TOR?

Factors Affecting NAPL Dissolution

- Groundwater velocity
  - Hydraulic conductivity
  - Hydraulic gradient
  - Porosity
- Sorption
  - Fraction of organic carbon
  - Partition coefficient
- Dispersivity
- Biodegradation (source area)

NAPL Composition



NAPL Constituent	Mass Fraction (g/g)
Benzene	0.01
Toluene	0.08
Ethyl benzene	0.05
Xylene	0.12
Other Aromatics	0.1
Aliphatics	0.55
MTBE	0.03
Inert	0.06

Raoult's Law

$$S_{ls}^{eq} = f_{ls} S_{ls}^{sol}$$

NAPL Constituent	Aqueous Solubility (g/m³)	Molecular Weight (g/mole)
Benzene	1780	78.1
Toluene	515	92.1
Ethyl benzene	140	106.2
Xylene	180	106.2
Other Aromatics	166	120.0
Aliphatics	12	97.0
MTBE	50,000	80.0
Inert	0	150.0

$$f_{ls} = \left(\frac{S_{ls}^{NAPL} / \omega_{ls}}{I^{NAPL} / \omega_I + \sum_{ls=1}^{NS} S_{ls}^{NAPL} / \omega_{ls} + \sum_{lt=1}^{NT} T_{lt}^{NAPL} / \omega_{lt}} \right)$$

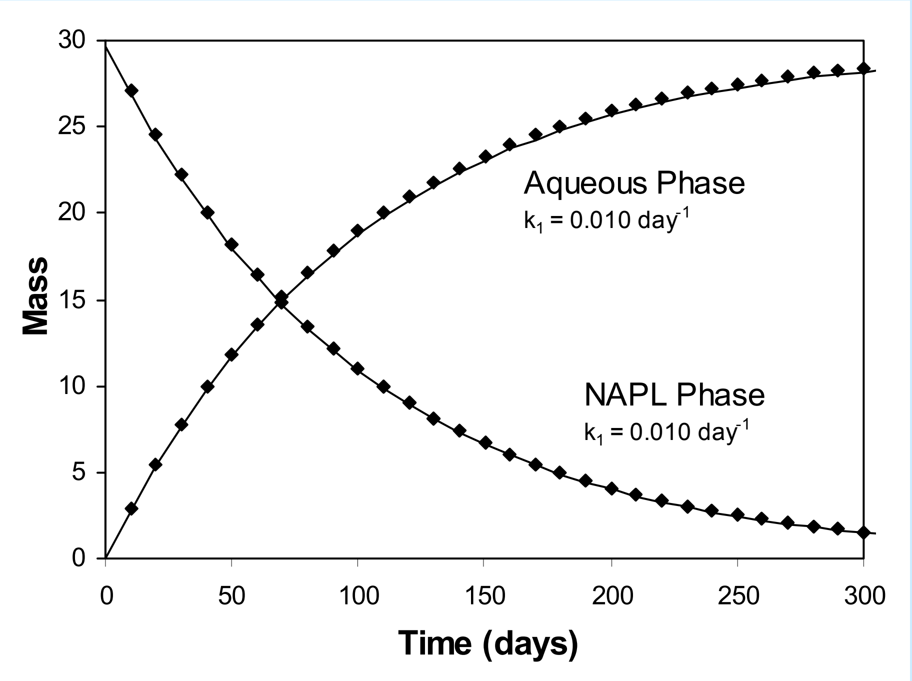
NAPL Dissolution

$$R_{source,ls}^{NAPL} = \max\left[0, k^{NAPL}\left(S_{ls}^{eq} - S_{ls}\right)\right]$$

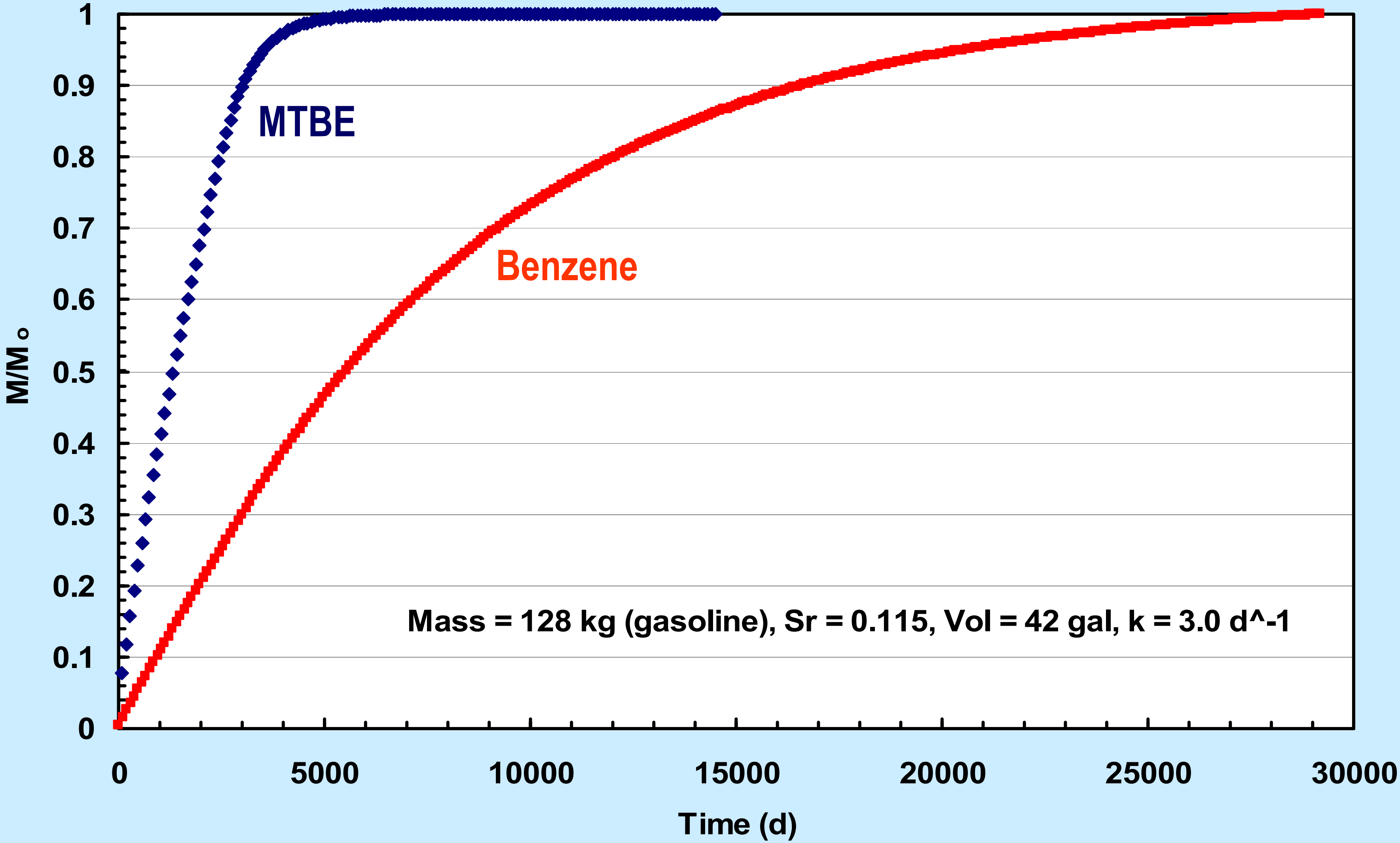
The rate of NAPL dissolution is specified using a mass-transfer function.

An equation of mass balance is written for the NAPL phase to account for source depletion.

$$\frac{dM_{ls}^{NAPL}}{dt} = -\theta k^{NAPL}\left[S_{ls}^{eq} - S_{ls}\right]$$



NAPL Dissolution



Estimating Source Mass

Inverse modeling

- Flux method by Butcher and Gauthier (*Ground Water*, v. 32, no. 1, 1994)
  - Estimate of source zone mass flux is developed using field data set, C(x,y), and 2D, steady-state analytical model
  - Flux estimate is matched to an analytical dissolution flux model by which NAPL volume or mass is quantified
- Compare numerical model results to time series data at source zone monitoring wells

NAPL Dissolution Demonstration

Open NAS and give demonstration of NAPL dissolution using Kings Bay data set

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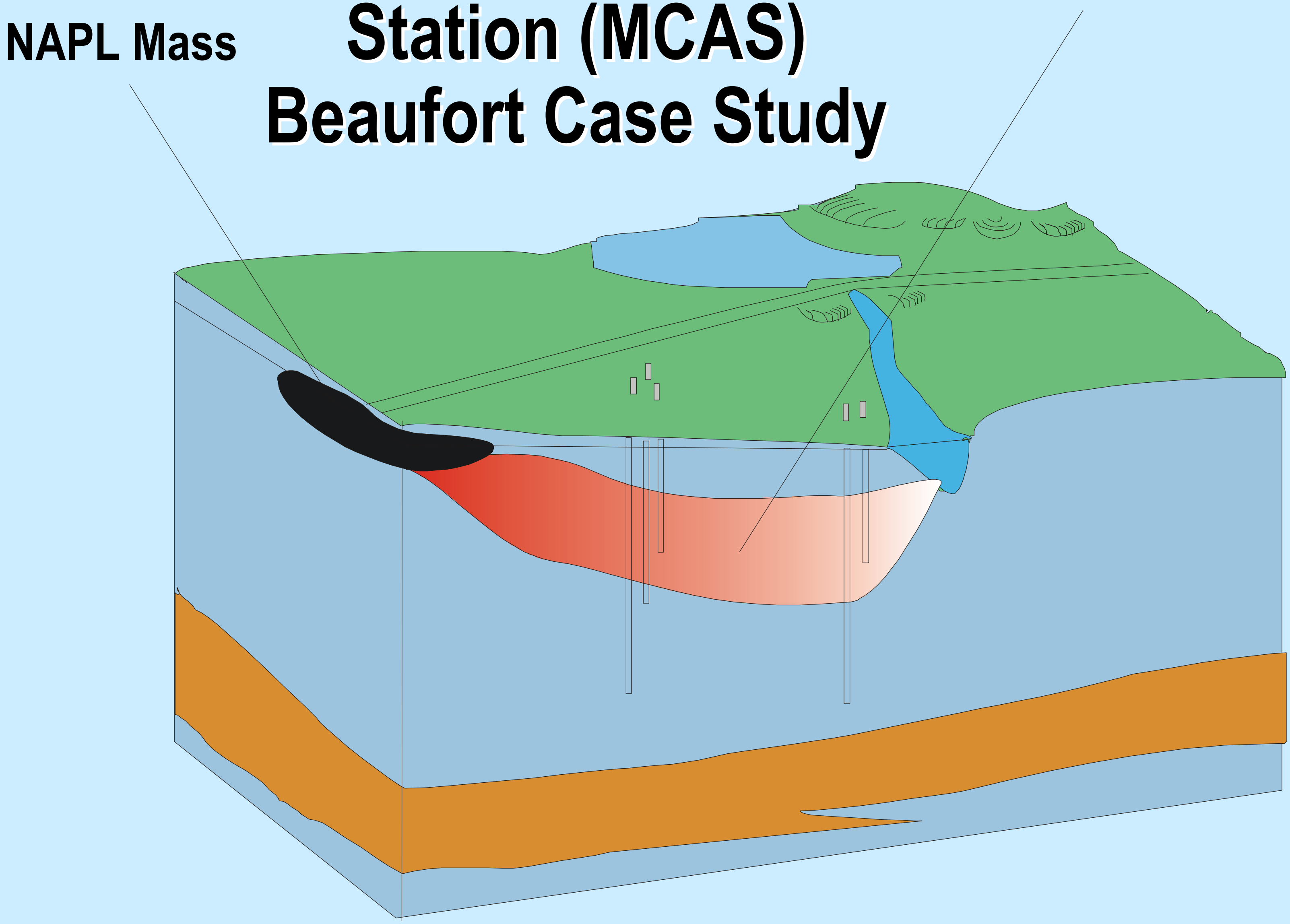
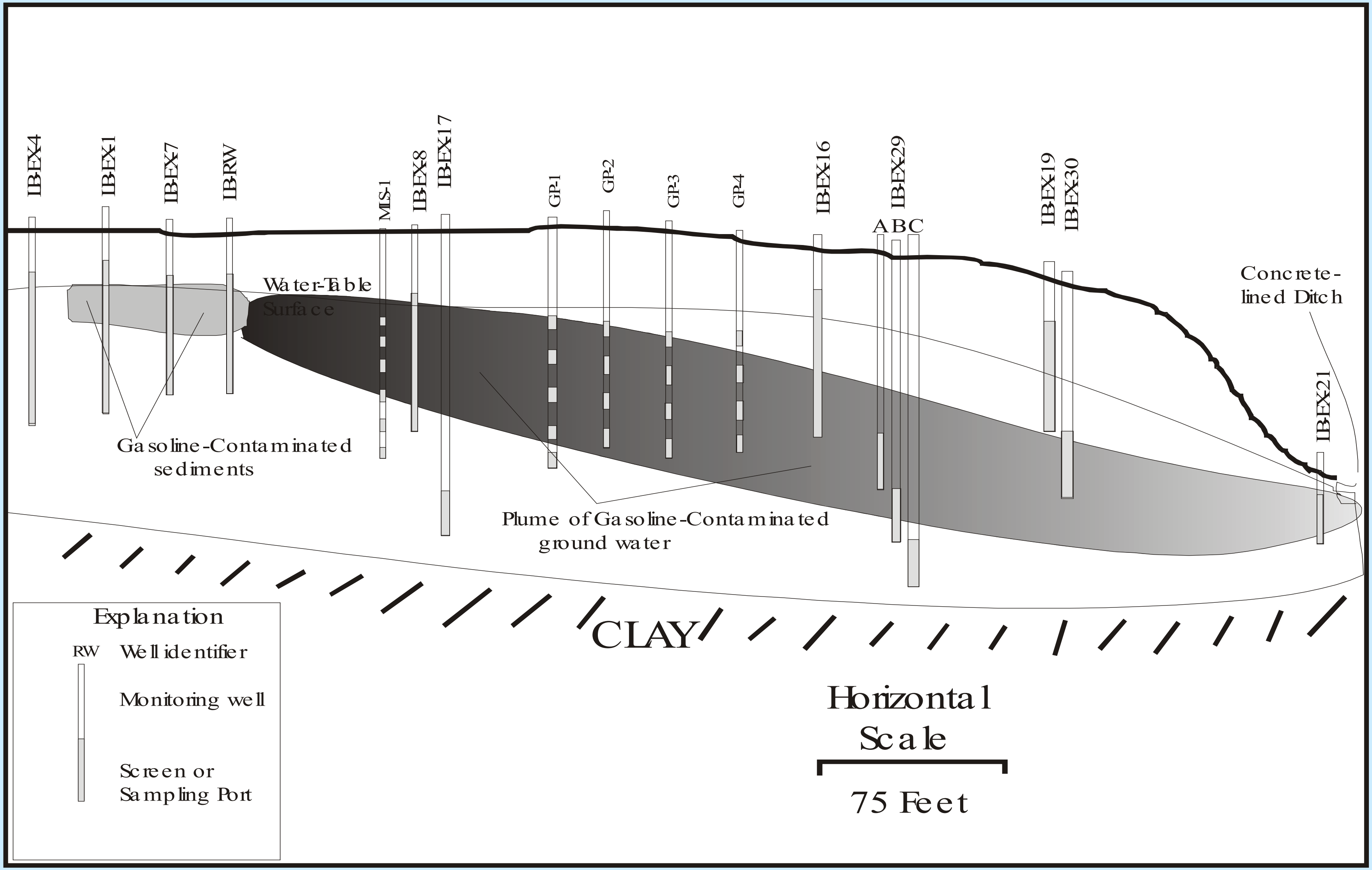
Marine Corps Air Station (MCAS) Beaufort Case Study

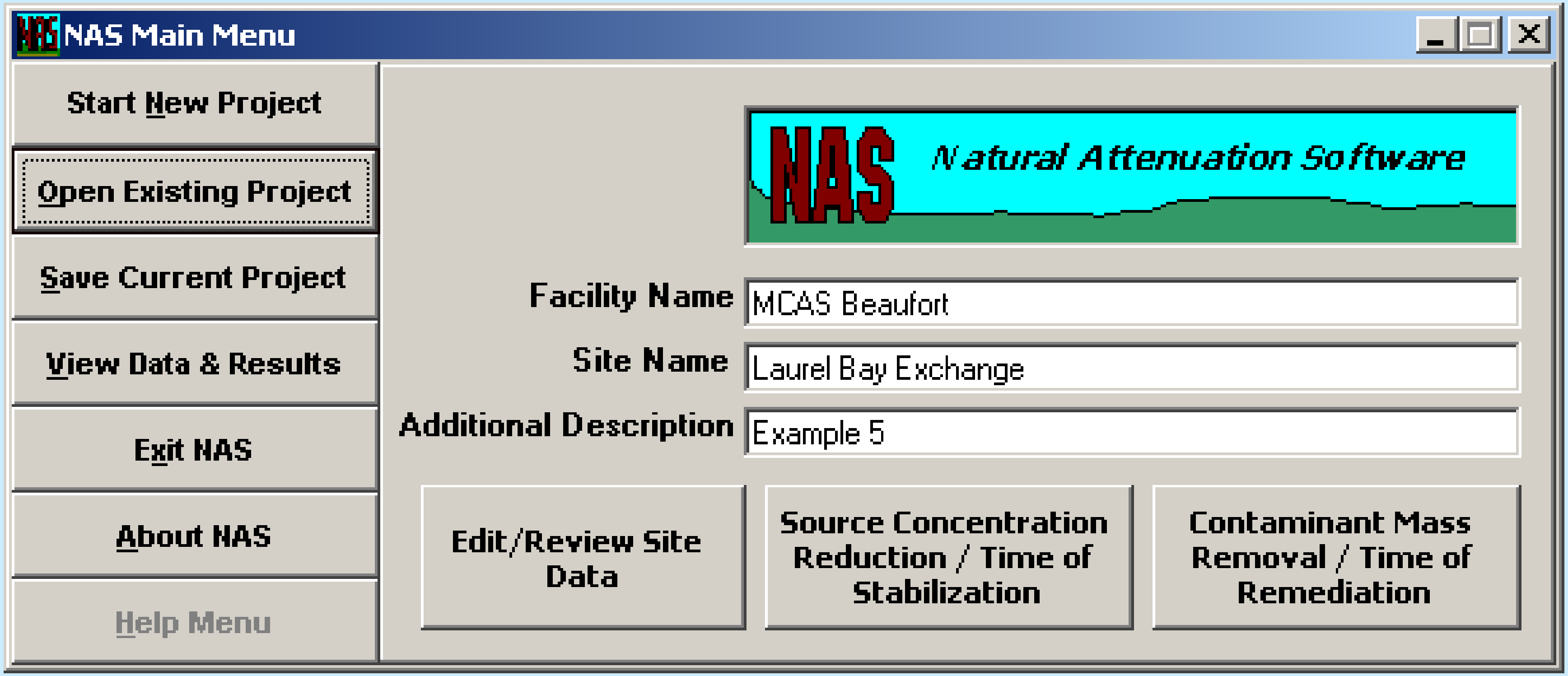


Laurel Bay Site, SC

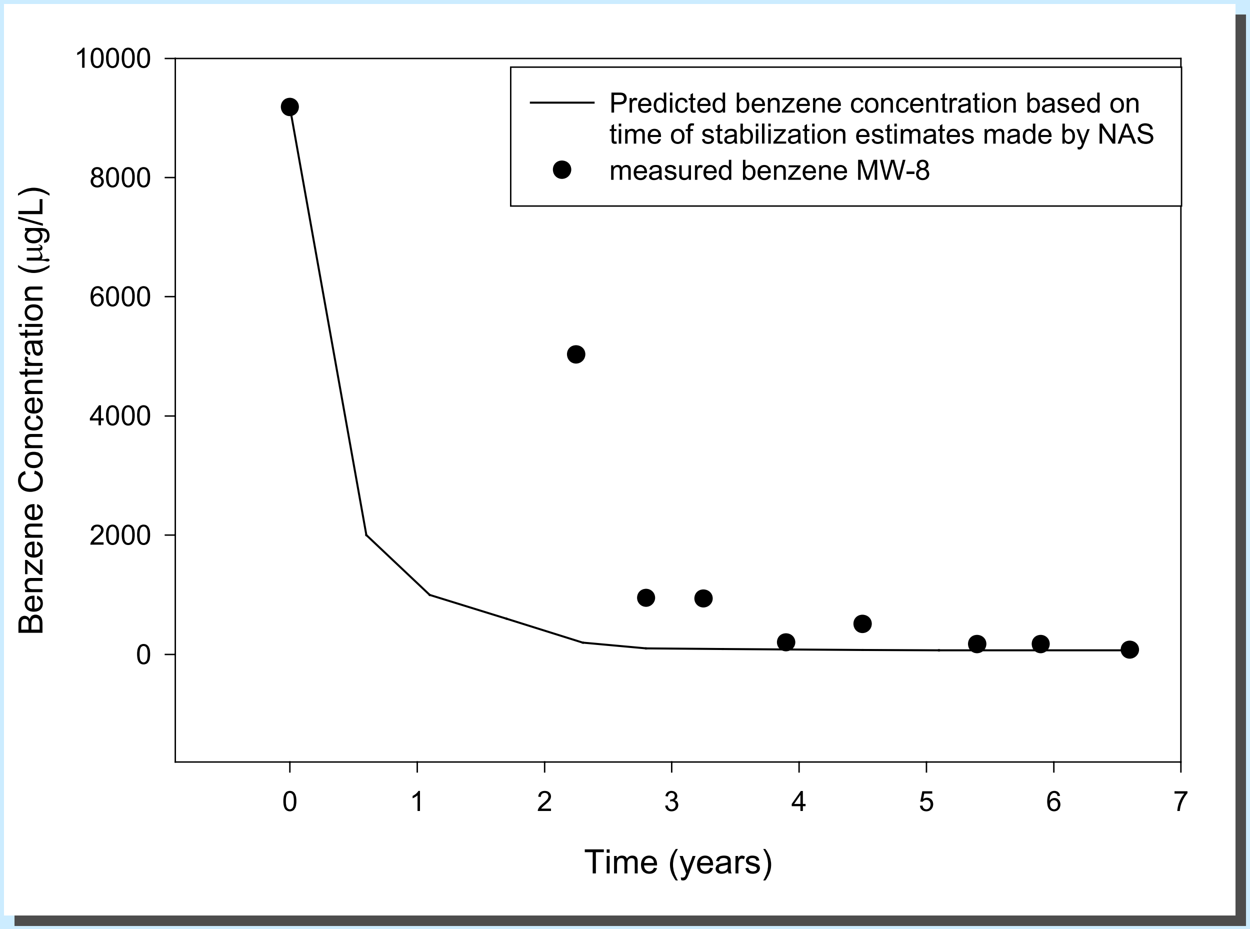


Natural Attenuation Software (NAS)

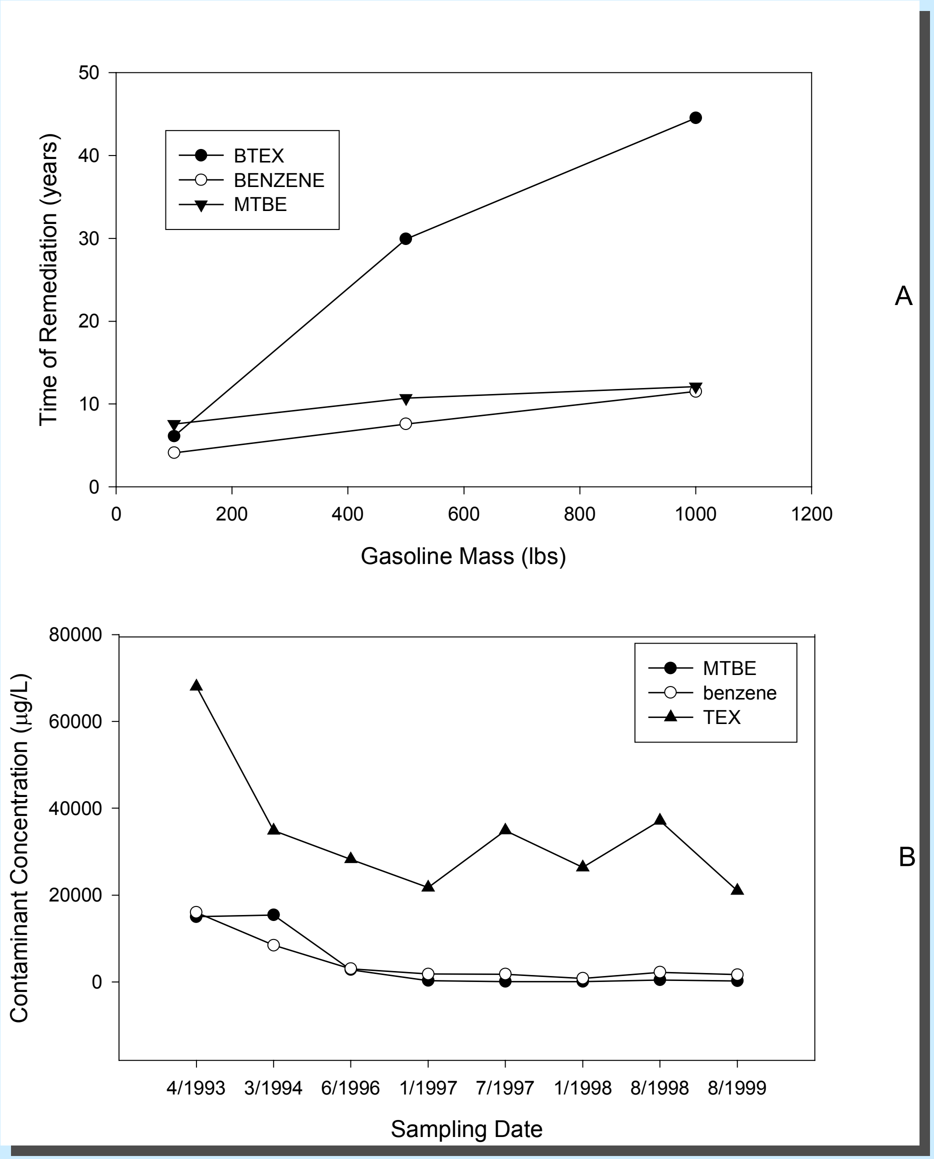
Laurel Bay Site



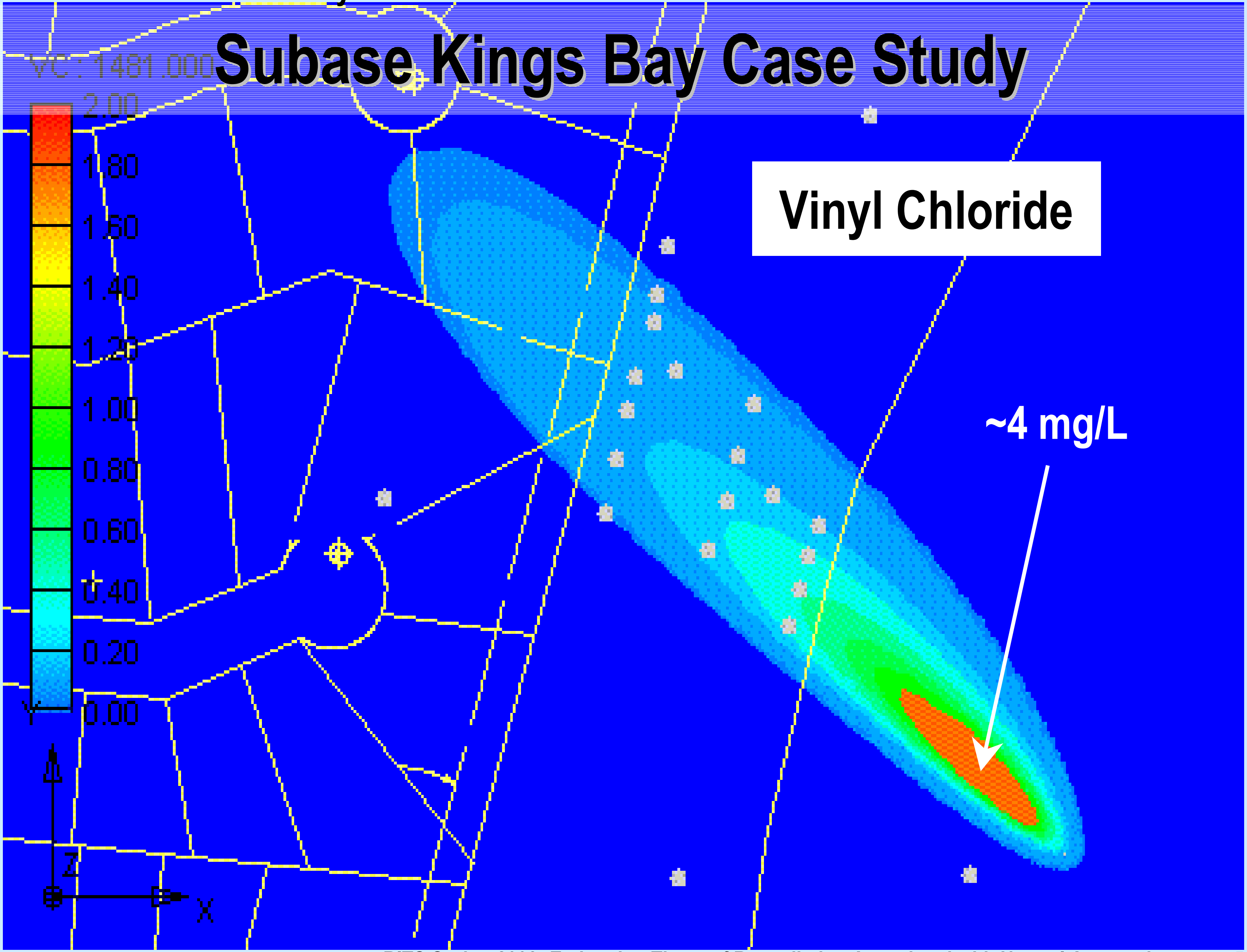
Time of Stabilization at Laurel Bay



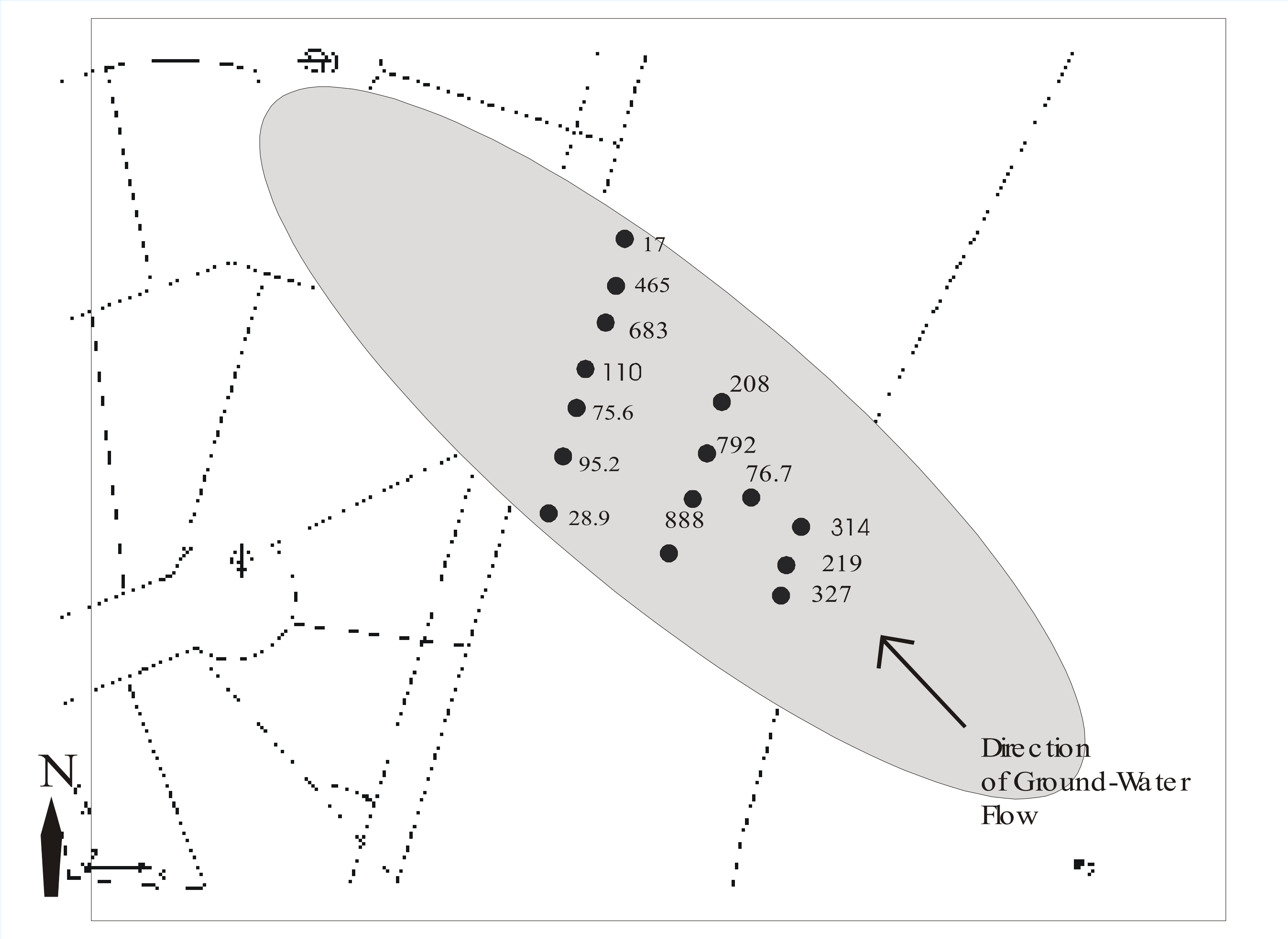
NAPL Dissolution TOR, MCAS Beaufort, SC



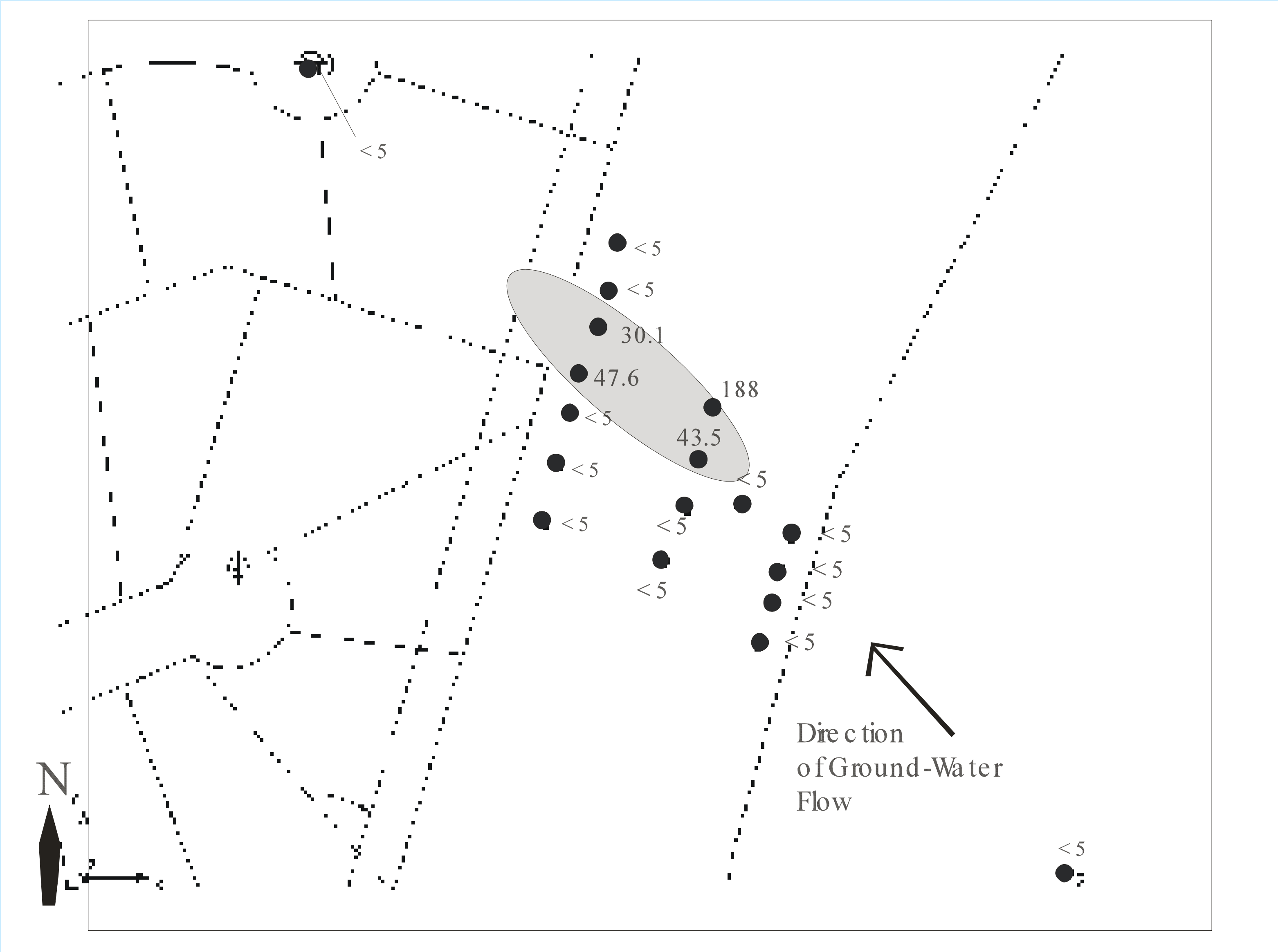
Subbase Kings Bay Case Study



Kings Bay Site, August 1998



Kings Bay Site, August 2002



Source Area
Before and After Fenton's Treatment

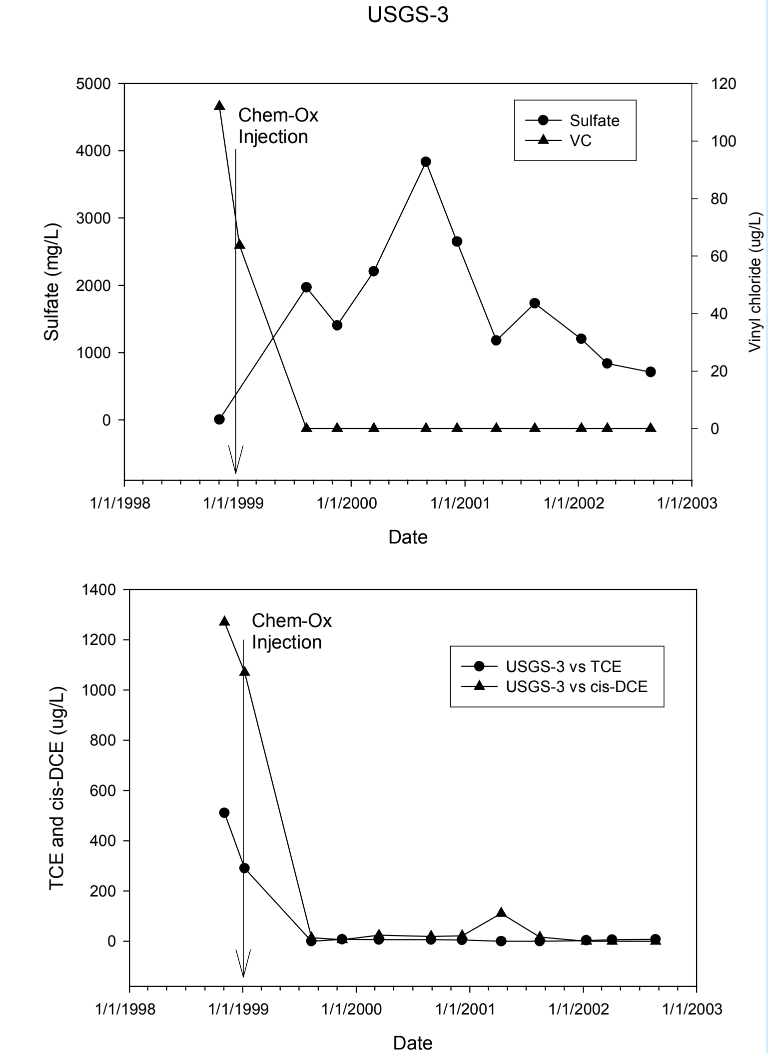


Figure --. Sulfate and chlorinated ethenes, USGS-3

KBA-13A
Before and After Fenton's Treatment

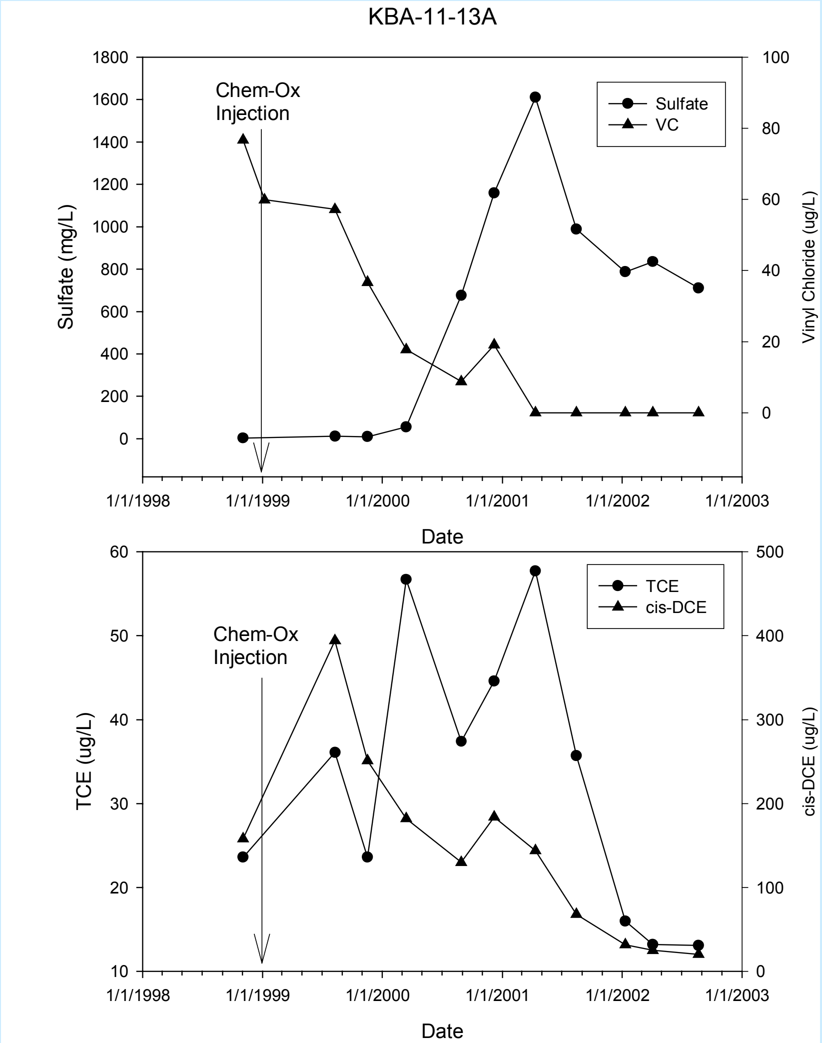


Figure --. Concentrations of sulfate, and chlorinated ethenes versus time after in-situ oxidation.

USGS-9

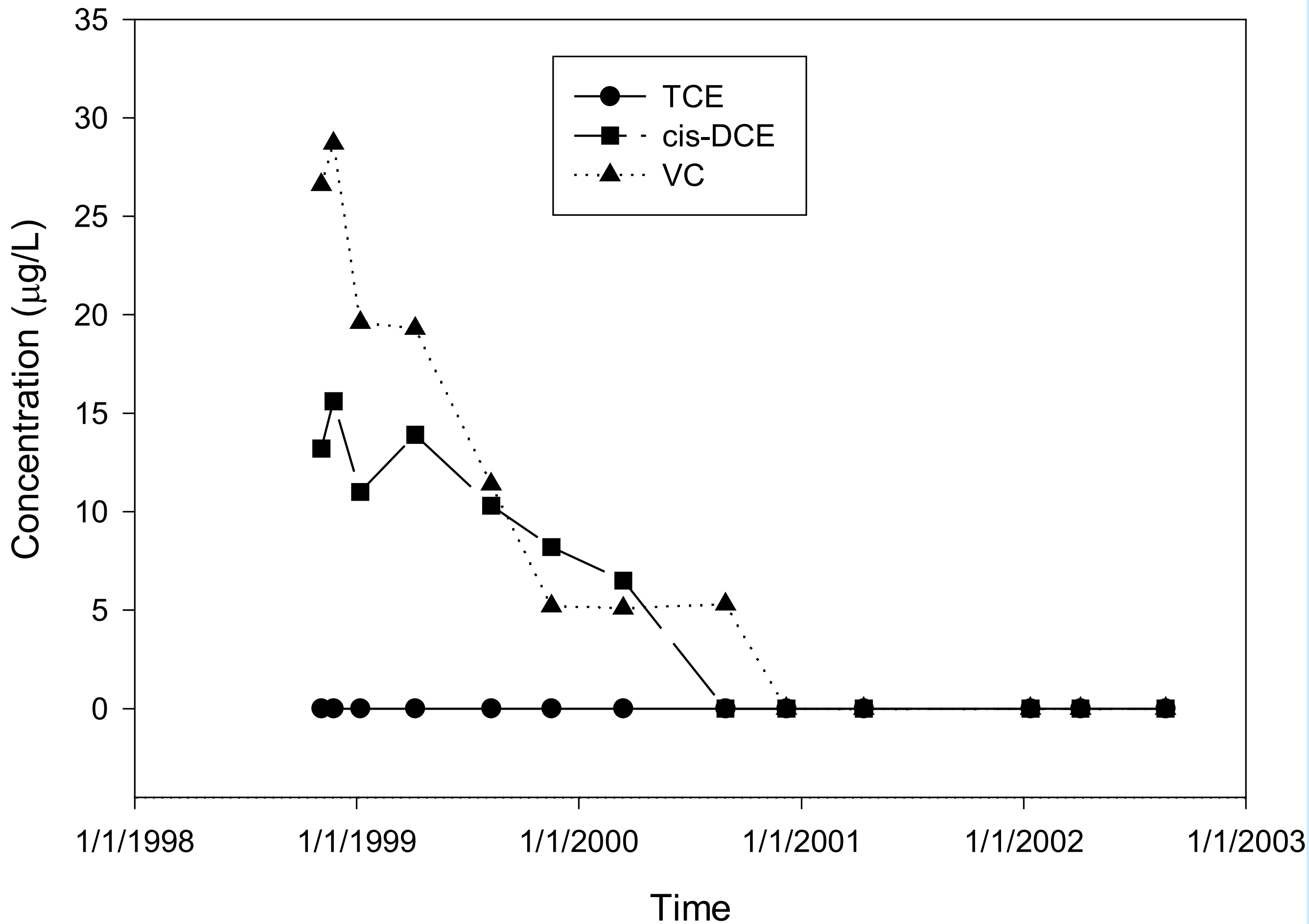


Figure 9.--Changes in concentrations of chlorinated ethenes at well USGS-9 between 1998 and 2002.

USGS-11

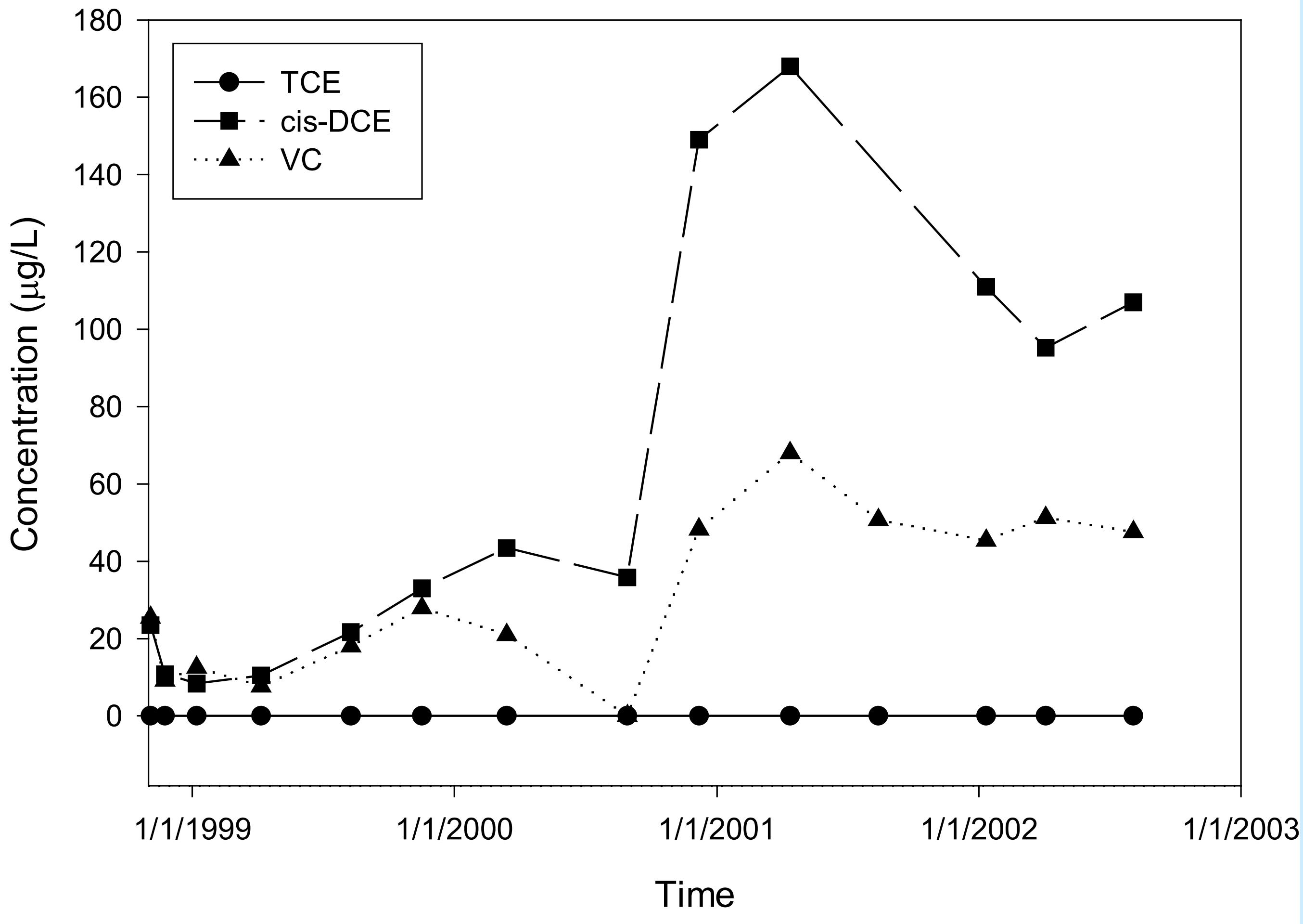
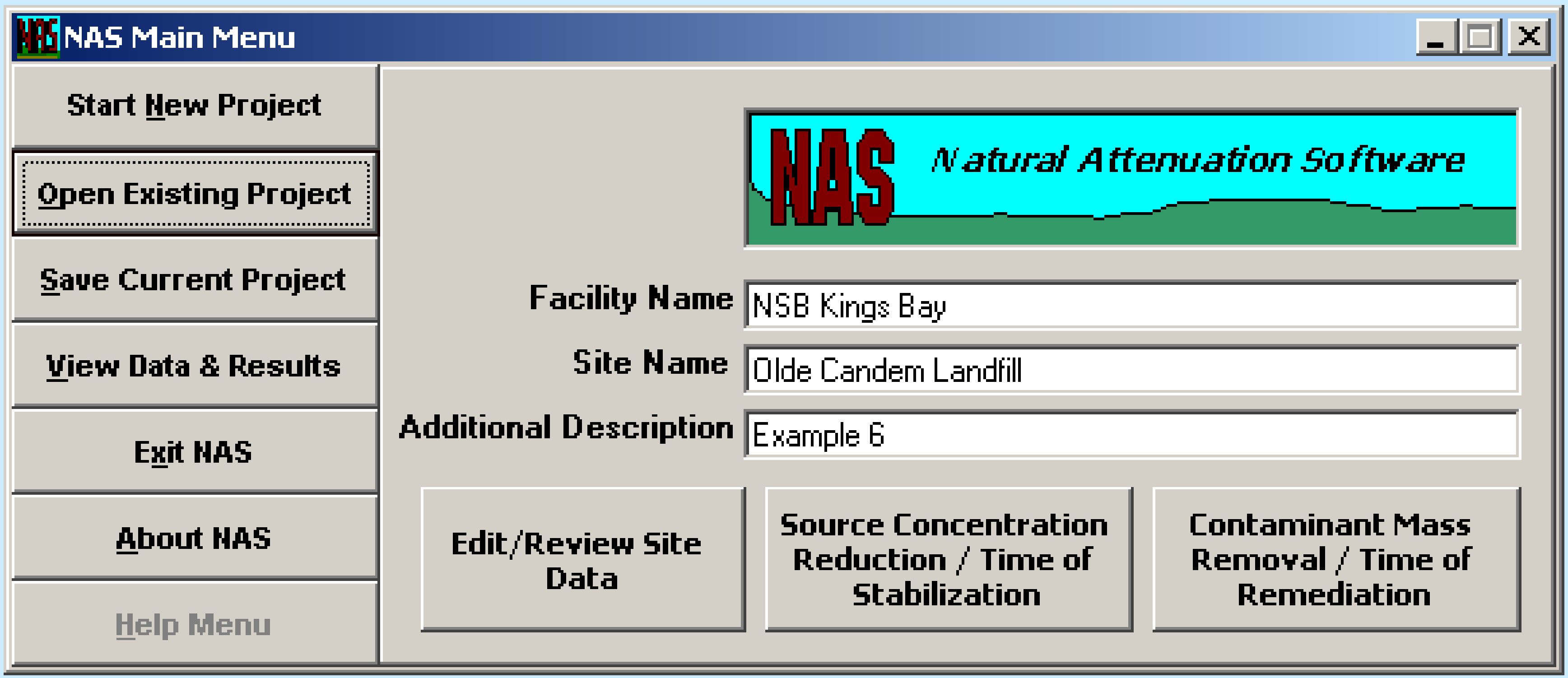


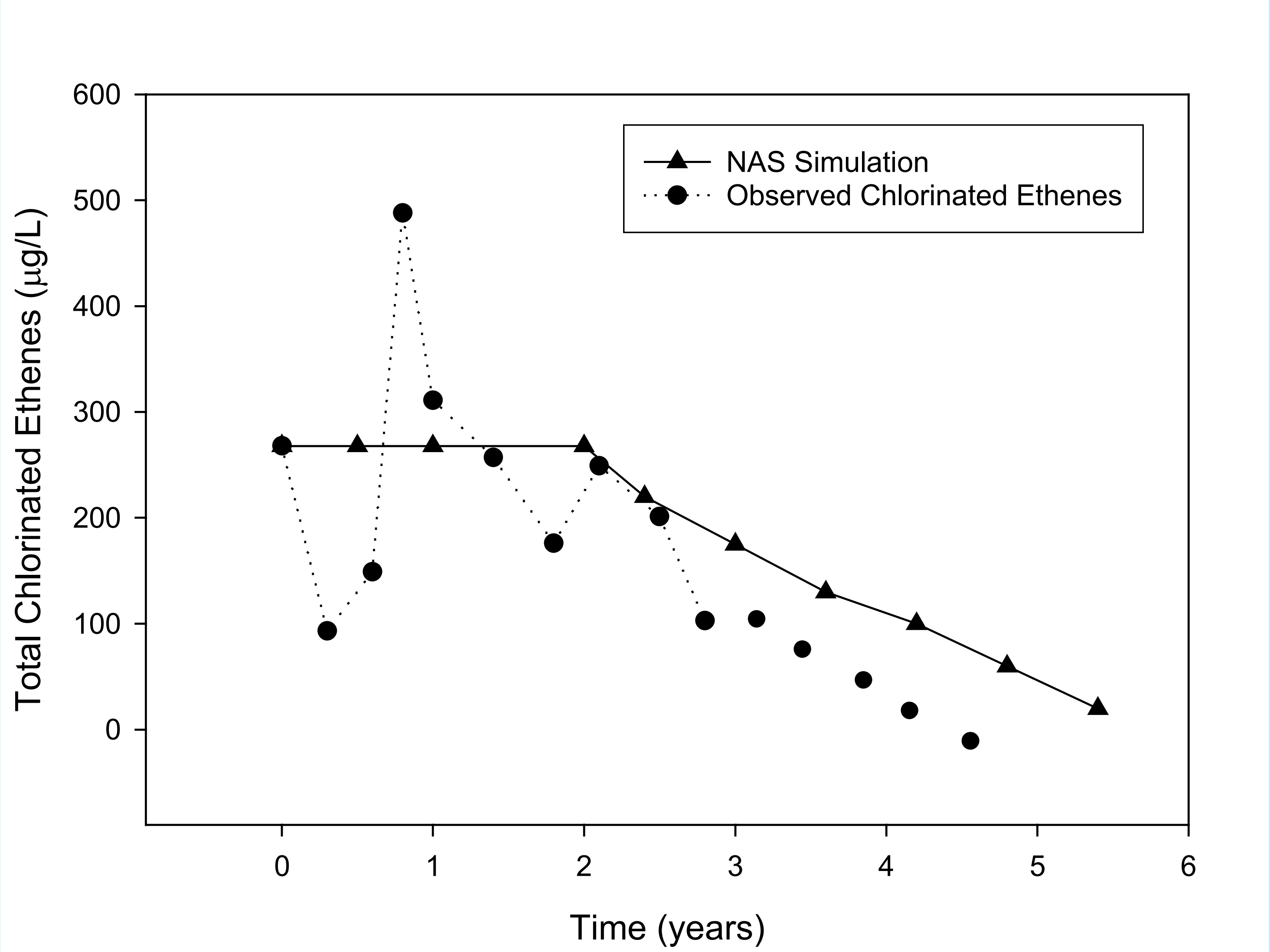
Figure 9.--USGS-11, Chlorinated Ethenes vs. Time (downgradient line of wells).

Natural Attenuation Software (NAS)

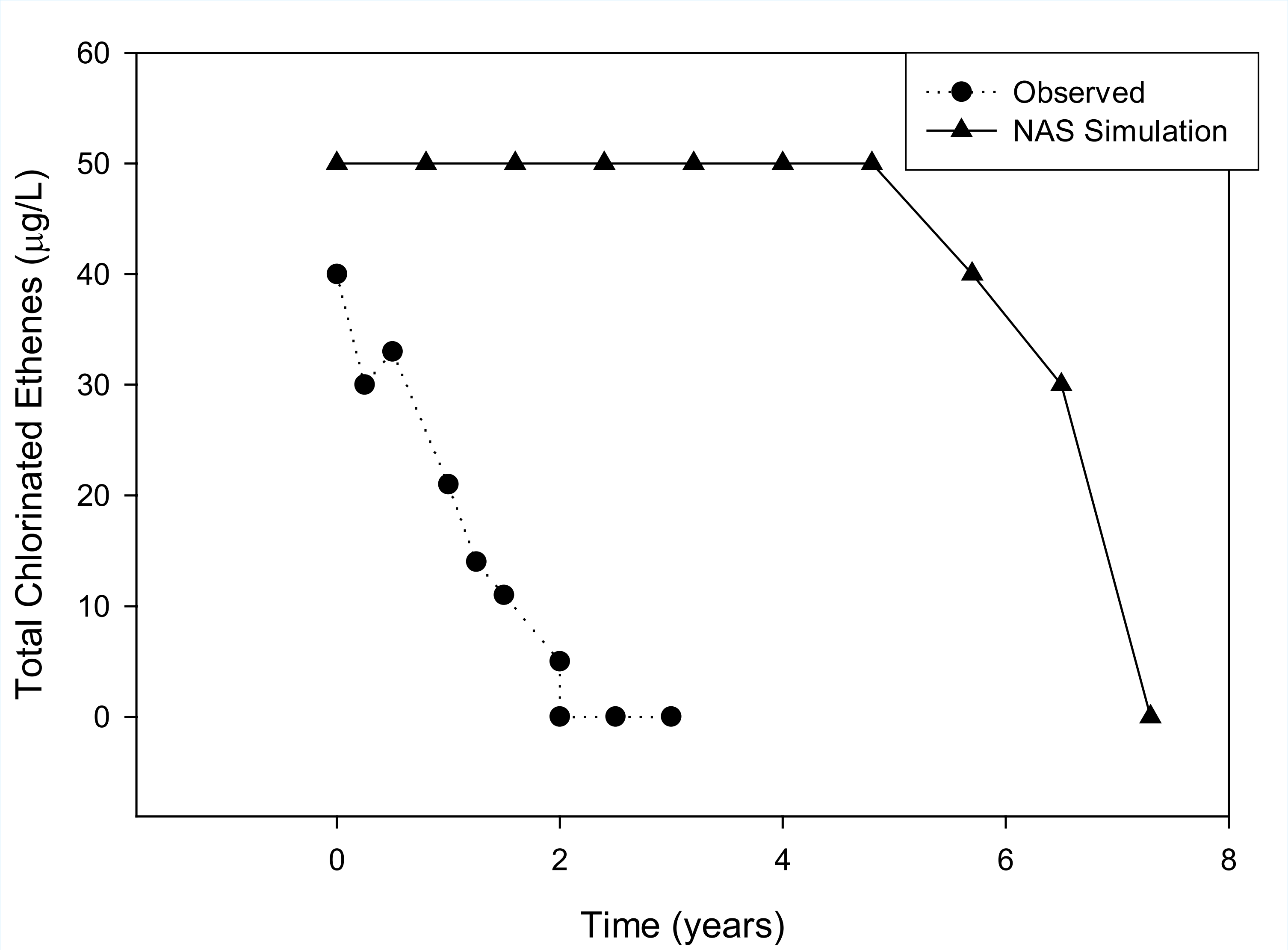
Kings Bay Site



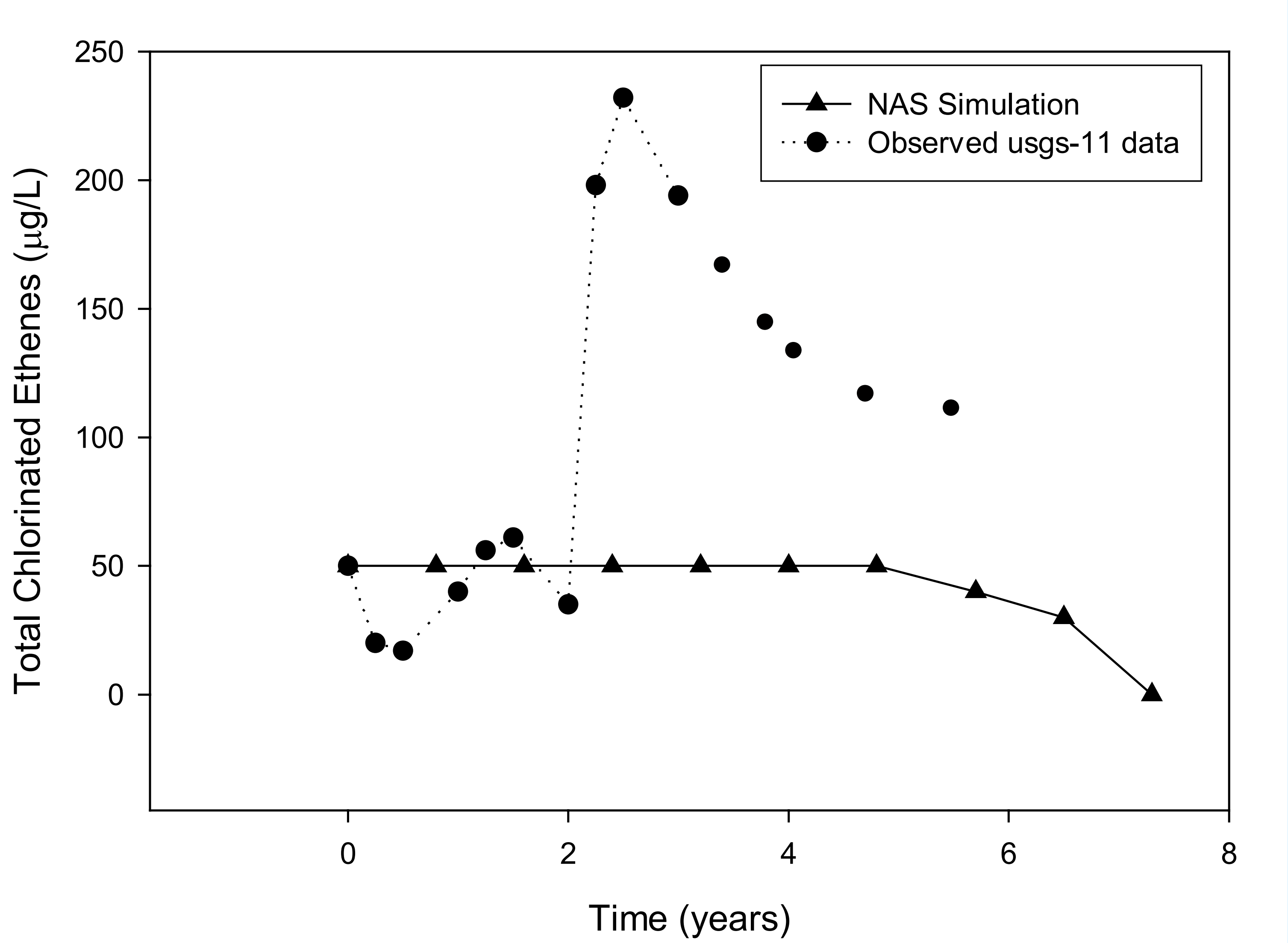
NAS Simulation of KBA-13A



NAS Simulation of USGS-9



NAS Simulation of USGS-11



Presentation Overview

- Introduction
- A Decision-Making Tool for Assessing MNA and Estimating Cleanup Times: Natural Attenuation Software (NAS)
- NAPL Dissolution Modeling with Sequential Electron Acceptor Model for 3D Transport (*SEAM-3D*)
- Case Study
- Conclusions

Conclusions

- The TOR problem is difficult but not unsolvable
- It is useful to divide the TOR problem into three interactive components
  - Distance of Stabilization (DOS)
  - Time of Stabilization (TOS)
  - Time of NAPL Dissolution (TNAD)
- The NAS tool uses this framework to facilitate TOR estimates
- NAS predictions are in line with monitoring data
- NAS has been used to reach regulatory closure of sites

NAS and *SEAM-3D* Software

- Acquiring NAS and SEAM-3D
  - NAS can be downloaded from: http://www.cee.vt.edu/nas/
  - *SEAM-3D* is part of Groundwater Modeling System (GMS) maintained by DoD
- Two-Day In-Depth Training for NAS
  - Southwest Division, July 22-23; Southern Division, August 5-6
  - Sign up through Engineering Service Center (ESC)

NAVFAC Points of Contact

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